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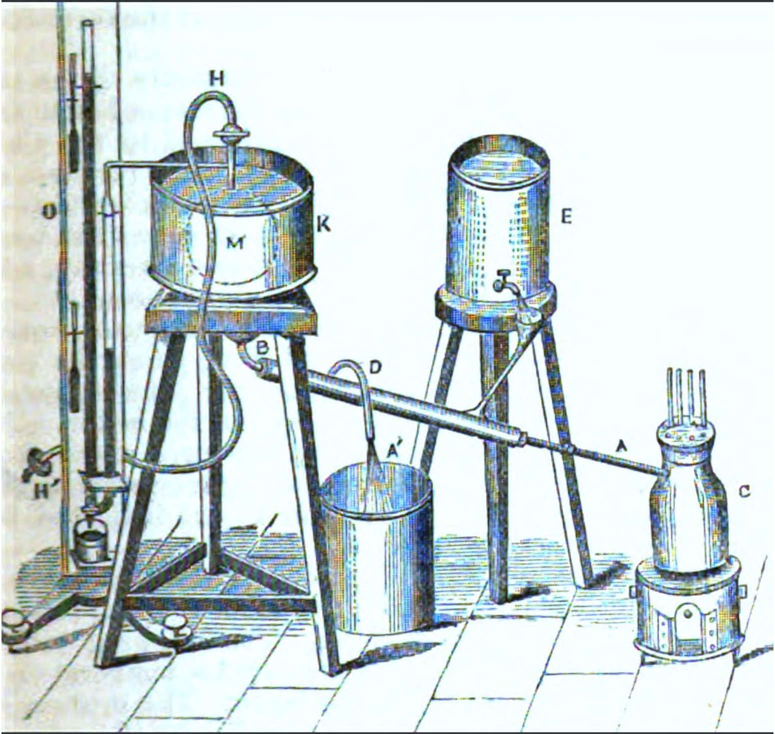

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Robert Galloway

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THE

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BY

ROBERT GALLOWAY, F.C.S.,

PROFESSOR OF PRACTICAL CHEMISTRY, MUSEUM OF IRISH INDUSTRY; AUTHOR OF "A MANUAL OF QUALITATIVE ANALYSIS," "THE FIRST STEP IN CHEMISTRY," ETC.

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PREFACE.

THIS work, as the title indicates, is not intended for the mere beginner; the subjects which ought to be brought before the student in a first book or course on the science having formed the subject of a former work, "The First Step in Chemistry," have therefore been omitted. It is intended to teach the higher branches of the science, especially those newer views which are now being very generally adopted. As these newer views are mainly founded on volume relations, the work commences by teaching the specific gravity of gases, and their correction for temperature, pressure, and moisture—combination by volume—the specific gravity of vapours, and its application to control the formulæ of substances—atomic volumes, &c.,—*by exercises*, which the student has to perform. These subjects, which I in common with most other teachers, I believe—have found it so difficult to make the student fully understand, I can state, from experience, can be taught with perfect success from the plan here developed. Instead of making the student accept the facts and principles on the *ipse dixit* of the book, the different views which are entertained by different chemists on the same subject are collated, and the several arguments by which these views are maintained are given so as to teach him to form his own opinion on the disputed points, rather than adopt the opinions of others; this method of teaching will best fit the student for reading original memoirs on the science, whilst, at the same time, from its exercising his reasoning faculties, it will form the very best discipline for the mind. I have therefore drawn largely upon original memoirs, and on such important subjects as molecular atoms, the doubling of the atomic weights of oxygen, sulphur, &c., I have not hesitated to give the memoirs of Sir B. Brodie, Dr. Wolcott Gibbs, and Dr. Odling, almost *in extenso*.

The history of the rise and progress of the new views is given, commencing with Dr. Clarke's and Mr. Griffin's views on the constitution of some compounds, passing on to the unitary system of Gerhardt, Williamson's views on the constitution of bodies, Laurent's views on the constitution of the ammonias, and, finally, Gerhardt's system of classification. Inorganic and organic bodies are then arranged under the different types, and an outline of the general properties of organic bodies is also given. This part of the book is founded upon the chemical functions of bodies in the fourth volume of Gerhardt's "Traité de Chimie Organique," but I think it will be found that in every part I have made it more systematic and more comprehensive. Under the ammonia type will be found, I trust, a full and accurate description of the beautiful and laborious researches of Hofmann on that class of bodies. I have intended this part of the book to form a *practical* and *systematic* manual of organic chemistry. I have also placed before the student the views of Wurtz, Playfair, Frankland, and Kolbe, on the constitution of bodies.

I have entered very fully into subjects which are daily becoming of much practical importance, such as fractional distillation, the law and method of determining the boiling points of liquids, the specific and atomic heats of bodies, the development of heat by chemical action, calorific intensity, &c. These subjects are taught, wherever practicable, by *exercises ;* finally, I have placed before the student a complete account of Graham's researches on diffusion, and Bunsen and

Kirchoff's on spectrum analysis. At the end of the book will be found a selection of questions by various examining bodies, and it is indicated by reference where the information may be found which will enable the questions to be answered.

I believe, with the exception of a few typographical errors, the work will be found as free as possible from errors inseparable from a work like the present, and for this I am greatly indebted to my friend, Mr. W. Plunkett, who very kindly assisted me in reading the proofs.

R. GALLOWAY.

DUBLIN, *December*, 1863.

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THE SECOND STEP IN CHEMISTRY.

CHAPTER I.

PROPERTIES OF MATTER.

Specific gravity of gases and vapours, 1. *Exercises. Expansion of matter by heat*, 5. *Correction of gases for temperature*, 12. *Exercises. Compressibility of matter*, 16. *Elasticity of matter*, 25. *Correction of gases for pressure*, 42. *Exercises. Liquefaction*, 43. *Vaporization*, 45. *Correction of gases for the tension of aqueous vapour. Exercises.*

1. Specific Gravity of Gases and Vapours.—Gases and vapours differ in their densities, or specific weights.

2. Atmospheric air, at 60° F., and the barometer standing at 30 inches, is employed as the standard of comparison[*] for gases and vapours. One hundred cubic inches of air weigh, according to the latest researches by Regnault, 30·935 grains *at this temperature and pressure*. Air is therefore about 814 times lighter than water, as 100 cubic inches of water weigh 25246·0 grains.

3. *If the specific gravity of a gas or vapour be known, the absolute weight of a given volume of it can be determined.* To accomplish this, we have simply to multiply the weight of an equal volume of air by the specific weight of the gas or vapour; the product will be the weight of the volume, at the standard temperature and pressure of the gas or vapour.

Example.—What is the weight of 100 cubic inches of hydrogen, its specific gravity being ·0694?

30·935 × ·0694 = 2·147 grains weight of 100 cub. in. of H.

4. *If it be desired to find the volume of a given weight*

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[*] The standard temperature and pressure adopted on the Continent differs from that employed in England. The temperature is 0° C. = 32° F.; the pressure is 760 millimetres = 29·922 inches.

of any gas or vapour, the weight of some volume (say a cubic inch) of the gas or vapour must first be ascertained by the preceding rule; then the given weight must be divided by the weight of the cubic inch; the quotient will be the volume in cubic inches of the given weight of the gas, at the standard temperature and pressure.

Example.—What is the volume of 2·147 grains of hydrogen, its sp. gr. being 0·0694?

$$\frac{2{\cdot}147}{{\cdot}02147} = 100 \text{ cubic inches.}$$

EXERCISES.

1. What is the weight of a cubic inch of oxygen, its sp. gr. being 1·1057?
2. What is the weight of a cubic inch of nitrogen, its sp. gr. being 0·9713?
3. What is the weight of a cubic inch of carbonic acid, its sp. gr. being 1·529?
4. What is the weight of a cubic inch of gaseous ammonia (NH_3), its sp. gr. being 0·59?
5. What is the volume of 54 grains of chlorine, its sp. gr. being 2·44?
6. What is the volume of 45 grains of carbonic oxide, its sp. gr. being 0·967?
7. How many cubic inches of oxygen would be obtained from 100 grains of chlorate of potash?

Oxygen gas is frequently prepared by igniting peroxide of manganese. The following decomposition occurs:—

$$3\,Mn\,O_2 = Mn_3\,O_4 + 2\,O.$$

8. How many cubic inches of oxygen would be obtained from 400 grains of a manganese ore containing 70 per cent. of the peroxide, the equivalent of manganese being 27·6?

Gunpowder consists of a mixture of carbon, sulphur, and nitrate of potash. The gunpowder which is most powerful as a propelling agent, is found to be that which corresponds most nearly in composition to the formula,— $K\,O, N\,O_5 + 3\,C + S$.

The theoretical decomposition of a powder of this description would be represented by the equation,—

$$KO, NO_5 + 3C + S = KS + 3CO_2 + N.$$[*]

In practice, it is found that small quantities of many other products are invariably formed besides CO_2, N, and KS[†]; among which may be mentioned carbonic oxide, hydrosulphuric acid, bisulphide of carbon vapour, carbonate of potash, cyanide and sulpho-cyanide of potassium, and aqueous vapour.

9. How many cubic inches of gas would be produced, at the standard temperature and pressure, from 1,000 grains of gunpowder, having the above composition, according to the theoretical decomposition?

5. **Expansion of Matter by Heat.**—All solid, liquid, and gaseous substances expand when they are heated, and contract when they are cooled; and the rate and degree of expansion of each substance is always the same, no matter how often it may be heated, if its temperature be the same at the commencement of each experiment, and the same amount of heat be added. For example,—if a substance at the temperature of 40° F. be heated up to 100° F., it will always expand to the same bulk when raised from 40° to 100° F., and it will always contract to the same bulk when cooled down again to 40° F.[‡]

6. The same amount of heat affects matter in its three states very unequally. It produces the greatest expansion in gases, and the least in solids, because there is no cohesiveness between the particles of matter in the gaseous state; the heat has, therefore, no opposing force to overcome; and as the cohesive force is less in liquids than in solids, a less amount of heat is neutralized in overcoming this opposing force, and, therefore, for the same amount

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[*] The gases disengaged in the combustion of this powder would occupy, at 32° F., a volume 329 times that occupied by the powder; but at the moment of ignition, the volume of gas is 2,000 times that of the powder, on account of the enormous heat. The temperature evolved by the combustion of gunpowder has been found sufficiently intense to fuse gold and other metals. It is estimated at 2192° F.

[†] The sulphide of potassium is, to a great extent, volatilized by the heat resulting from the explosion of the powder, and the highly heated vapour ignites as it passes into the air, becoming converted into sulphate of potash. The white smoke observed on the ignition of powder is produced in this way.

[‡] Lead is an exception to the rule; "it is so soft, that its particles slide over each other in the act of expansion, and do not return to their original position. For example,—a leaden pipe used for conveying steam permanently lengthens some inches in a short time; and the leaden flooring of a sink which often receives hot water, becomes, in the course of time, thrown up into ridges and puckers."—*Graham.*

of heat, a greater expansion takes place in liquids than in solids.

7. All gases, on account of the absence of any cohesiveness between their particles, *expand alike*,[*] the pressure being the same, for equal additions of heat; and contract alike for equal subtractions of heat; but the different liquids and solids expand and contract unequally, for equal additions and subtractions of heat.

8. Having stated that all gases expand and contract alike, on account of the absence of any cohesiveness between their particles, the following law, "that the rate of expansion for all gases is equal and uniform at all degrees of heat,"[†] might even be inferred.

9. Gases expand rather more than one-third their volume on being raised from the temperature at which ice melts to that at which water boils, at the ordinary atmospheric pressure; one volume of any gas, at the temperature of melting ice, expands to 1·3665[‡] volumes, if its

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[*] All that is stated in this and the adjoining pages, with respect to gases, applies also to vapours, at some distance above their points of condensation.

[†] This law was discovered by Gay Lussac and Dalton.

[‡] It is necessary to observe, before proceeding further, that this uniform dilatation of all gases is not absolutely true. The more condensable gases display irregularities, especially near their points of solidification and liquefaction. Regnault and Magnus have published independent and elaborate investigations on the expansion which various gases undergo by the application of heat. According to their experiments, the coefficient of expansion is not rigidly uniform for all gases, the expansion being greatest for those which are most readily condensable; whilst for the gases which have resisted all efforts to liquefy them, scarcely any appreciable differences are observed. Although it is not, therefore, rigorously true that all gases, and likewise vapours, at some distances above their points of condensation, expand alike, yet it is sufficiently accurate for all the requirements of chemistry.

The following table contains a summary of Regnault and Magnus's experimental results.

EXPANSION OF GASES BY HEAT.

1000 Parts, at 32° F., become	At 212° F.	
	Regnault.	Magnus.
Hydrogen	1366·13	1365·659
Carbonic Oxide	1366·88	
Atmospheric Air	1367·06	1366·508
Nitrogen	1366·82	
Hydrochloric Acid	1368·12	
Carbonic Acid	1370·99	1369·087
Protoxide of Nitrogen	1371·95	
Cyanogen	1387·67	
Sulphurous Acid	1390·28	1385·618

temperature be raised to that of boiling water. If, then, the interval from the melting point of ice to the boiling point of water were divided into 100 degrees, any gas which measured one volume at the melting point of ice would increase ·003665 in bulk for each degree it increased in temperature. In France, and on the Continent generally, the scale of the thermometer is divided in this way, it is, therefore, called the Centigrade scale; the temperature at which ice melts is reckoned 0°, and the temperature at which water boils at the standard pressure is represented as 100°; therefore, any gas which measures one volume at 0° of the Centigrade scale will measure 1·003665 in bulk at 1° C., 1·00733 at 2° C., and so on: for every degree it increases or decreases in temperature by the Centigrade scale, it increases or decreases in bulk ·003665.

10. In England and America, Fahrenheit's scale is principally employed; the interval between the melting point of ice and the boiling point of water, according to this scale, is divided into 180 degrees; 32° on this scale is the temperature at which ice melts, 212° that at which water boils at the standard pressure. As one volume of gas at 32° F. expands to 1·3665 at 212° F., it results that for each degree Fahrenheit that the gas increases in temperature it must increase in bulk ·00204, for

$$\frac{\cdot 3665}{180} = \cdot 00204;$$

and as one volume of gas increases ·00204 in bulk for each degree Fahrenheit, 490 volumes of gas must increase one volume for each degree F. that it increases in temperature.

11. As gases expand equally at all degrees of heat, it is not necessary, when taking the specific gravity of a gas, to conduct the operation at a particular temperature, as we are obliged to do when taking the specific gravity of solids or liquids; it is only necessary to note the temperature of the gas at the moment the experiment is made; we are then able to calculate the volume it would occupy at the standard temperature. It is also necessary to know how to compute the volume a gas would occupy at some other temperature than that at which it is measured, for other purposes besides determining the specific gravities. We will therefore explain how the calculations are made, and give a few exercises which the student must perform.

12. *Correction of gases for temperature.—To calculate the volume of a gas from a lower to a higher temperature on the Fahrenheit scale,* we multiply the number ·00204, which is the amount one volume of any gas expands for each degree F., by the difference between the thermometric degree at which the gas is measured, and that at which we desire to find the volume, and to the product thus obtained we add 1 for the volume unit. Suppose, for the sake of illustration, we wanted to know what volume a gas, measured at 32° F., would occupy at 50° F., we multiply ·00204 by 18 = (50° F. — 32° F.), and to the product we add 1 for the volume unit, which gives 1·03672 volumes. A gas which measured 1 volume at a temperature of 32° F. would expand to 1·03672 volumes when raised to the temperature of 50° F.; we then multiply the number we thus obtain, which in our illustration is 1·03672, by the number of volume units the gas measured at the lower temperature, this will give us the volume the gas we have measured would occupy at the higher temperature. In our example the lower temperature is 32° F., and the higher temperature is 50° F., and suppose the gas measured 20 cubic inches at 32° F., we should consequently have to multiply 1·03672 by 20; the product would be the volume the 20 cubic inches, the gas measured at 32° F., would occupy at 50°F.; thus,—

$1{\cdot}03672 \times 20 = 20{\cdot}7344$, the number of cubic inches the gas measured at 50° F.

The following is a general form for these calculations:—let v denote the known volume, and v_1 the unknown volume; let t denote the temperature of the known volume, v, and t_1 the temperature of the unknown volume, v_1, the formula is,—

$$v_1 = v \times \left\{1 + {\cdot}00204 \times (t_1 - t)\right\}$$

13. *To reduce the volume of a gas from a higher to a lower temperature on the Fahrenheit scale,* the number of volume units the gas measures at the higher temperature must be divided by the number obtained by multiplying ·00204 by the difference between the thermometric degree at which the gas is measured, and that at which we desire to find the volume, and adding to the product 1 for the volume unit, the quotient will be the volume the gas will occupy at the lower temperature. As an example, we

will reverse our former illustration. What volume will 20·7344 cubic inches of gas, at 50° F., occupy at 32° F.?

$$\frac{20·7344}{1 + ·00204 \times 18} = 20 \text{ cubic inches.}$$

The general formula would be,—

$$v_1 = \frac{v}{1 + ·00204 \times (t - t_1)}$$

14. Or the calculation may be made in the following way:—490 volumes of a gas at 32° F. would increase 18 volumes if its temperature was increased to 50° F. (10); therefore, a gas which measured 490 volumes at 32° F. would measure 508 volumes at 50° F. The volume, therefore, of any gas at 32° F., would bear the same proportion to the bulk which it would occupy at 50, as 490 does to 508, and hence,—

$$490 : 508 :: 20 : 20·7346.$$

The general formula would be,—

$$v_1 = \frac{v \times [490 + (t_1 - t)]}{490}$$

If, instead of calculating the volume of a gas from a lower to a higher temperature, we were by this plan to reduce the volume from a higher to a lower temperature, the calculation would be as follows, if we reversed our former illustration, viz., What volume will 20·7346 cubic inches of gas, at 50° F., occupy at 32° F.?

$$508 : 490 :: 20·7346 : 20 \text{ cubic inches.}$$

The general formula would be,—

$$v_1 = \frac{v \times 490}{490 + (t - t_1)}$$

15. The calculation would be much the same if we used the centigrade, in place of the Fahrenheit, division; the principal difference would be that we should have to substitute ·003665 for ·00204, as ·003665 is the amount gases expand for every degree centigrade.

The following would be the general formula for calculating the volume of a gas from a lower to a higher temperature, according to the centigrade scale:—

$$v_1 = v \times (1 + ·003665 \times t)$$

The following would be the general formula for reducing the volume of a gas from a higher to a lower temperature, according to the centigrade scale:—

$$v_1 = \frac{v}{1 + \cdot003665 \times t}.$$

EXERCISES.

10. A gas measures 20 cubic inches at 50° F. What would it measure at 60° F.?
11. A gas measures 15 cubic inches at 90° F. What would it measure at 60° F.?
12. A gas measures 7·3 cubic inches at 180° F. What would it measure at 60° F.?
13. A gas measures 100·3 cubic inches at 40° F. What would it measure at 60° F.?
14. A gas measures 10·7 cubic inches at 320° F. What would it measure at 80° F.?
15. A gas measures 15 cubic inches at 0° C. What would it measure at 60° C.?
16. A gas measures 40·1 cubic inches at 100° C. What would it measure at 0° C.?
17. A gas measures 3·5 cubic inches at 0° C. What would it measure at 80° C.?

16. COMPRESSIBILITY OF MATTER.—All solid, liquid, and gaseous substances admit, on account of their porosity, of compression; that is to say, their volume can be reduced by pressure without diminishing their *mass*, in other words, the number and size of their material particles.

17. "Some of the metals have their bulk permanently diminished by hammering. When metals are melted together in the formation of alloys, there is often great contraction. Equal bulks of tin and copper are found to undergo a contraction amounting to the fifteenth part of their volume."

18. Liquids were long considered to be incompressible; but it has not only been proved that they are compressible, although they admit of very slight compression,—but even the degree of compression which some liquids experience has been estimated. For every additional atmosphere, as it is called, or pressure of 15 lbs. on the square inch, water is compressed rather more than 46 millionths

of its volume; alcohol 21, and ether 61 millionths of their respective volumes.

19. Gases admit of the greatest compression. "If we take a metal cylinder, closed at one end, and insert an accurately-fitting piston into the other, it will be impossible to force the piston into the tube, if it be full of water; but if full of air, the force of the arm is sufficient to drive the piston down so as to reduce the volume of the air ten or twenty times. If the piston be small, we feel the resistance increase in proportion to the compression; and, whatever force is exerted, we cannot make the piston touch the bottom of the tube, because, in order to do that, the air must lose its impenetrability, or, in other words, be annihilated. When the pressure is removed, the air regains its original bulk, which is not the case with metals, and some other solids, after they have been strongly compressed."—*Tomlinson.*

20. The law which connects the volume of a gas with the pressure made upon it, may be thus expressed.

The volume of a gas is inversely as the pressure to which it is exposed; that is to say, if the pressure be doubled, the *volume* is reduced one-half; if the pressure be trebled, the volume is reduced to one-third, and so on. This law was discovered independently by Boyle, in England (1661), and Marriotte, in France (1684): it is generally called Marriotte's Law. This law can be demonstrated by the apparatus (Fig. 3), which was devised by Marriotte himself, and is therefore known under the name of the tube of Marriotte.

21. Many gases have been liquefied by exposing them to the pressure of their own atmospheres. The difference between gases and vapours is therefore merely one of degree. Although "some few of the gases have still resisted the best advised attempts to liquefy them, it can hardly be doubted that all gases may be regarded as the vapours of liquids of an extremely high degree of volatility, the liquids resulting from the condensation of gases boiling at temperatures far below the ordinary atmospheric range. Vapours, on the contrary, may be considered as the gases of liquids of comparatively low volatility."—*Miller.*

22. Faraday, who was the first to liquefy gases, adopted a very simple method of proceeding; the materials were sealed up in a strong narrow tube, of the form shown in Fig. 1. The gas, being disengaged by the application of

heat or otherwise, accumulated in the tube, and by its own pressure brought about the condensation.

"In order to estimate the degree of pressure which the condensed gas exerted upon the interior of the vessel in which it was contained, and to determine the force requisite to overcome the repulsive energy of its own particles, Faraday made use of small air-gauges, which he enclosed in the tubes employed for the condensation.

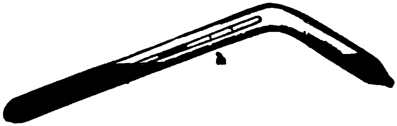

Fig. 1.

"These gauges consisted of a somewhat conical, capillary tube of glass, which was divided into parts of equal capacity, by introducing into the tube a globule of mercury, shown at *a*, and causing it to occupy each part of the tube in succession. The length of the little cylinder into which the mercury was reduced in each portion of the tube, was marked upon the glass with black varnish. The mercury was then transferred towards the widest extremity, and the tube was sealed at its narrow end. A known volume of air was thus included, and by the compression which this air experienced in the course of the experiment, the bulk being inversely as the pressure, the elastic force of the gas under examination was easily calculated." By this means, Faraday liquefied the gases named in the subjoined table; the table gives the pressure in atmospheres, and the temperature at which the condensation took place:—

	Atmospheres.	Temperatures, F.
Sulphurous acid	2	45°
Sulphuretted hydrogen	17	50
Carbonic acid	36	32
Chlorine	4	60
Nitrous oxide	50	45
Cyanogen	3·6	45
Ammonia	6·5	50
Hydrochloric acid	40	50

23. Mr. Faraday has also liquefied olefiant gas, hydriodic and hydrobromic acids, phosphuretted hydrogen, and the gaseous fluorides of boron and silicon. But, in order to liquefy these, he had to adopt a different method. He employed, in this case, narrow green glass tubes of great strength, powerful condensing syringes, and an extremely low temperature. The low temperature was produced by a mixture of solid carbonic acid and ether. The temperature of this mixture in the air, measured by a spirit thermometer, was found to be −106° F.* Under these circumstances, the liquefied hydriodic, hydrobromic, and sulphurous acid gases, carbonic acid, nitrous oxide, sulphuretted hydrogen, cyanogen, and ammonia, froze to colourless transparent *solids;* and alcohol became thick and oily. Oxygen, hydrogen, nitrogen, nitric oxide, carbonic oxide, and coal gas, did not liquefy at the temperature of −166° F., while subjected to pressures varying from 27 to 58 atmospheres. M. Natterer has since succeeded in liquefying nitrous oxide gas by means of a condensing pump, and without the use of strong frigorific mixtures.

24. It may be observed, in conclusion, that some gases may be liquefied by the mere reduction of temperature without the aid of pressure. Sulphurous acid is liquefied by reducing the temperature to 0° F.; and Faraday, by means of the mixture of carbonic acid and ether, liquefied, without the aid of pressure, chlorine, cyanogen, ammonia, sulphuretted hydrogen, arseniuretted hydrogen, hydriodic acid, hydrobromic acid, and carbonic acid.

25. ELASTICITY OF MATTER.—Solid bodies have a *fixed form;* liquids and gases have not, they always assume the form of the vessel which contains them.

26. The *volume* of a liquid is fixed, but that of gases and vapours is not; their volume is only determined by the sides of the vessels containing them. This tendency of gaseous bodies to diffuse themselves in all directions distinguishes them from liquids, which have only a lateral extension; gases also admit of great, liquids of very slight, compression. This tendency of gases to extend in every

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* When the same mixture was placed beneath the receiver of an air-pump, and exhaustion rapidly made, the temperature sunk to −166° F.

direction, is owing to the gaseous particles being governed solely by the repulsive power of heat. This expansibility of gases is termed their *elastic force*. It is their chief physical peculiarity; and as they possess it in the very highest degree, they are frequently called *elastic fluids*.

27. The resistance which a substance offers to the compressing force, is termed its elasticity. "Elasticity, in its widest sense, is applied to the tendency the particles of matter have to preserve a certain *distance* or *position* with regard to each other, and resume that distance or position when disturbed therefrom. In *gases* and *liquids*, this applies only to the *distance*, and not to the *position* of the particles; for they have no tendency to assume one position in preference to another. This tendency is the peculiar characteristic of *solids*, in which we accordingly distinguish not only the elasticity of *compression* (common to all bodies), but also three other kinds of elasticity not found in liquids and gases, viz., those of *tensure*, *flexure*, and *torsion;* for the various ways in which we can alter the form or dimensions of a body, may all be reduced to these four modes,—*squeezing*, *stretching*, *bending*, and *twisting;* but only the first of these is applicable to liquids and gases.

28. "In no solids, however, is any one of these four kinds of elasticity found to be both perfect and unlimited. In some solids, such as glass, they all appear to be *perfect*, for no force, however great or long continued, causes glass to take a *set*, as it is called, that is, a permanent change either in form or bulk; but then, this elasticity is confined within narrow limits, on exceeding which fracture is the result. In those solids whose elasticity (of one or more kinds) is less limited, as in metals, or apparently unlimited (as in the flexure of India-rubber, or the torsion of a thread), the return of the particles to their previous position is only partial. There remains a permanent change of form, which is called a *set*."

29. Liquids possess a small but very perfect elasticity, which varies in amount in different liquids; the densest liquids, in general, being those which least admit of compression.

30. As the volume of any gaseous body is only deter-

mined by the sides of the vessels containing it, it follows that, if from a vessel filled with any gas, some of the gas be withdrawn, the remainder of the gas will expand until it has filled the vessel, *but* the pressure upon the sides of the vessel will be less after, than before, the partial removal of the gas; because the elastic force of gas diminishes with its expansion, and increases with its compression.

1. *The elastic force of a gas is directly as the pressure, and inversely as the volume.*
2. *The density of a gas is also directly as the pressure, and inversely as the volume.*
3. *And the volume of a gas, as before noticed, is inversely as the pressure.*

Example.—100 cubic inches of a gas, under a pressure of 30 inches of mercury, will expand to 200 inches if the pressure be diminished one-half, and it will occupy only 50 inches if the pressure be increased to 60. The change of density must necessarily be in the inverse proportion to that of the volume, and the elastic force follows the same rule.

31. The elasticity of gases, and the law by which it is regulated, admits of experimental proof. To understand the proof a knowledge of the pressure of the atmosphere is necessary; this must, therefore, be briefly described before explaining the experiment.

32. The air cannot have the same density throughout its height, because each layer of air-particles bears the pressure of the layers above it, but not of those underneath; therefore, the pressure must decrease on each ascending layer; the lowest layer will bear the pressure of all the rest; the one next above the lowest will bear the pressure of all but the layer underneath it; and the third lowest layer will bear the pressure of all but the two layers underneath it; and so on with the succeeding higher layers.

33. As the pressure on each ascending layer decreases, so the density must decrease, because *the density of a gas is directly as the pressure, and inversely as the volume.* The air decreases in density in the following progression; —at an elevation of 3 miles it is $\frac{1}{2}$ the density of the air on the earth's surface; at 6 miles it is $\frac{1}{4}$; at 9 miles $\frac{1}{8}$; and

at 15 miles $\frac{1}{30}$ of that density.* The air is supposed to extend 40 or 45 miles from the earth's surface; this, in all probability, is its utmost limit. "Dr. Wollaston has shown that, at this elevation, the attraction of the earth upon any one particle, is equal to the resistance arising from the molecular repulsive power of the medium. Another proof of the finite extent of the atmosphere is found in the fact of the sun and the planets being destitute of any similar media surrounding them; for if it is supposed to extend into infinite space, such large masses of matter as the planets must surely have caused a considerable portion to gravitate towards them. Other philosophers have supposed that the extreme cold of the upper regions is sufficient to prevent the infinite expansion of the atmosphere."

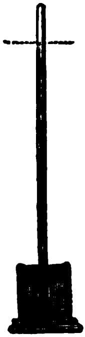
Fig. 2.

34. If a tube, about 33 or 34 inches in length, and closed at one end, either by means of a stop-cock, or else by being hermetically sealed, be carefully filled with mercury, so as to remove all traces of air, be then placed in an upright position, with its open end downwards, and dipping into a cistern of mercury (Fig. 2), the mercury will sink in the tube until it stands at about 30 inches above the level of that in the cistern; during the act of inserting the tube the open end is closed airtight with the finger, which is removed when that end of the tube is immersed in the mercury. That portion of the upper part of the tube which is unfilled with mercury is the nearest approach to a perfect vacuum which can be procured by art, for on

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* DENSITY OF THE AIR AT INCREASING ALTITUDES.

Height above the sea, in miles.	Bulk of equal weight of air.	Density.	Height of Barometer in inches.
0	1	1	30·00
3·4	2	$\frac{1}{2}$	15·00
6·8	4	$\frac{1}{4}$	7·50
10·2	8	$\frac{1}{8}$	3·75
13·6	16	$\frac{1}{16}$	1·87
17·0	32	$\frac{1}{32}$	0·93

The numbers in the first column form an *arithmetical* series, by the constant addition of 3·4; those in the second column an increasing *geometrical* series, each being double its predecessor; and those in the third and fourth, a decreasing geometrical series, in which each number is the half of that standing above it.—*Miller.*

lowering the tube deep enough into the cistern of mercury, the whole tube will become completely filled with the mercury; and on elevating the tube in the cistern the mercury again sinks in the tube. The vacuum thus obtained is termed the Torricellian vacuum, from its being first observed in 1663 by Torricelli, a pupil of Galileo. Although this is the most perfect vacuum that can be obtained, it is, nevertheless, not a perfect one, as the apparently empty space of the tube contains a *minute* quantity of mercurial vapour.

35. If the stop-cock at the closed end of the tube were opened, the mercury in the tube would sink down to the same level as the mercury in the cistern. This experiment proves that it is the pressure of the atmosphere on the surface of the mercury in the cistern that sustains or makes the mercury in the tube stand about 30 inches above the level of that in the cistern. Therefore, the pressure of the atmosphere at the sea level must be equal to the weight of a column of mercury about 30 inches in height, and the base of which is equal to the surface the air presses on. Now, a column of mercury about 30 inches in height, and having an area of one inch, weighs between 14 and 15 pounds; consequently, the pressure of the atmosphere at the sea level must be about 15 pounds upon every square inch of the earth's surface, and everything upon the earth. As the specific gravity of water is 13·59 times less than that of mercury, the atmosphere must sustain a column of water 13·59 times higher than that of mercury, because the two columns, although so disproportionate in height, would have the same weight. As the density of the atmosphere decreases as we ascend (33), the height of the mercurial column must also lessen as we ascend above the level of the sea. The barometer can, therefore, be employed to measure the heights o mountains, and other altitudes.

36. Not only does the pressure of the atmosphere decrease as we ascend from the level of the sea, but at the sea level the mean pressure of the atmosphere varies with the latitude. But in addition to these changes of atmospheric pressure with change of altitude or place, the pressure "at the same spot is liable, from a variety of causes, to continual variation. The average pressure at the sea level is equivalent to that of a column of mercury 30 inches in height; but in this climate it is sometimes so

diminished as to support a column of only about 28 inches; at other times, the pressure will be equivalent to 31 inches of mercury."—*Miller*.

37. If a square glass vessel be carefully closed at the neck, and placed under the receiver of an air-pump, on removing the external pressure, the vessel will be blown to pieces by the pressure or elastic force of the air inclosed within the vessel.

38. "We see, from this experiment, that a portion of air, cut off from all communication with the atmosphere, still exerts a pressure in all directions against the sides of the vessel containing it; and it can be proved that this internal pressure is exactly equal to the pressure which an equal surface undergoes from the weight of the external atmosphere. But this internal pressure cannot arise from the weight of the included air (for this is only a few grains); it must therefore arise from its elasticity, or expansive force, that is to say, the force with which it tends to expand to its natural bulk, or that bulk which it would occupy if subject to no pressure—if, for example, it were removed to the top of the atmosphere.

39. "The elasticity of air, and the law by which it is regulated, can be very well illustrated by means of a long bent glass tube (Fig. 3), open at its longer extremity, and furnished with a stop-cock at the shorter. The stop-cock being open, a quantity of mercury is poured into the open end. The surfaces of the mercury, A *a*, will, of course, stand at the same level in both legs. The two columns of air, A C and *a* D, sustain a pressure equal to the weight of a column of air continued from A and *a* to the top of the atmosphere. If we now close the stopcock, D, the effect of the weight of the whole atmosphere above that point is cut off, so that the surface, *a*, can sustain no pressure arising from the weight of the atmosphere. Still the level of the mercury remains the same, because the elasticity of the column of air, *a* D, is precisely equal to the weight of the whole column before this small length was cut off. The surface,

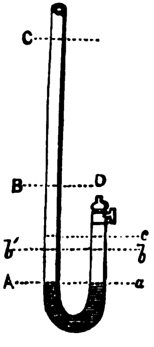

Fig. 3.

A, is still pressed by the whole atmospheric column, and thus we see that these two different properties of the atmosphere,* its *elasticity* and its *weight*, exactly counterbalance each other.

40. "Now we know that the atmospheric pressure, under ordinary circumstances, is equal to 14½ lbs. on the square inch, or to a column of mercury 30 inches high. It is evident, therefore, that the atmospheric pressure acting on A is the same as would be produced by a column of mercury, 30 inches high, resting on the surface of A. So, also, the force with which the air confined in *a* D, presses by its elasticity on the surface, *a*, is also equal to a column of mercury 30 inches high. The pressure of the atmosphere acting on the surface, A, is transmitted by the mercury to the surface, *a*, and balances the elastic force of the isolated column, *a* D.

41. "If we now pour an additional quantity of mercury into the open end of the tube at C, an increased pressure, arising from the weight of the metal, will be transmitted to the surface, *a*, and will prevail over the elasticity of the confined air; the surface, *a*, will therefore rise towards D, compressing the air into smaller space. On continuing to pour in mercury, until the surface, *a*, rise to *b*, or half-way between *a* and D, that is, until the confined air is compressed into exactly half its former limits, it will be found, on drawing a horizontal line from the surface, *b*, to the opposite *b'*, in the longer limb, that the column of mercury, *b'* B, measures exactly 30 inches, the weight of which is equal to the atmospheric pressure. The force with which the surface, *b*, is pressed upwards towards D, is therefore equal to *two atmospheres*, or double the force with which *a* was pressed upwards towards D. Hence it appears that the elasticity of the confined column of air, *b* D, is double its former elasticity when filling the space, *a* D; so that when the air is compressed into half its volume, its elasticity is doubled. If we again pour mercury into the tube at C, until the air enclosed in the shorter limb be reduced to a third of its bulk, as at *c* D, the compressing force will be equal to three times the atmospheric pressure. The height of the compressing

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* This applies not only to air, but to all gaseous bodies.

column of mercury would reach to C, namely 60 inches above the level, *c*. If we still add mercury, until the column rise to the height of 90 inches above its level in the short limb, the elastic force of the confined air would be four times greater than at first, and it would be compressed to the bulk of one-fourth of its original volume."* This experiment proves that *the elastic force of gases varies in exactly the same proportion as their density.*

42. *Correction of Gases for Pressure.*—At the moment a gas is weighed or measured, it is necessary to observe the height of the barometer, as this gives the pressure to which the gas is then subjected, provided the liquid over which the gas is collected stands on the *same level* both *in* and *outside* the vessel containing the gas. If, however, the liquid stands *higher* inside than outside the gas-vessel, the gas will be subjected to a pressure less than that of the atmosphere at the time, by the amount necessary to support the column of liquid above its outer level. If the liquid stands *lower* in the gas-vessel than outside, the gas is under greater pressure than that of the atmosphere by the amount of pressure which a column of the liquid, equal to the difference in its height, without and within the gas-vessel exercises. In this latter case, the perfect level of the liquid within and without the vessel may readily be restored by raising the gas-vessel. If the fluid stands higher within than outside the vessel, which is generally the case, it is rarely possible in practice to bring it to the same level. A correction has therefore to be made for this inequality of level, which is accomplished in the following way:—Suppose the gas to have been collected over mercury, in order to allow for the dilatation occasioned by the inequality of level, the difference of the two heights must be accurately measured, and the measurement so obtained must be subtracted from the height of the mercurial column in the barometer at the time. A similar correction is required if the gas be standing over water, but it is smaller in amount,—a column of water, 13·6 inches in height, being equivalent to one inch of mercury. When this correction has been made, a

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* Tomlinson's "Pneumatics."

simple calculation enables one to discover the volume any gas would measure at the standard pressure.

Example.—What volume would a gas, standing over mercury, measure at the standard pressure, which measures 60 cubic inches, the barometer at the time standing at 28·75, the level of the mercury *in* the gas-vessel being 1·5 inch higher than that *outside?* By Marriotte's law, the bulk of a gas is inversely as the pressure to which it is subjected. Therefore,—

Standard pressure.		Observed pressure.		Observed volume.		True volume.
30	:	28·75 — 1·50 = 27·25	::	60	:	54·5

EXERCISES.

18. What volume would a gas, standing over mercury, measure at the standard pressure, which measures 19 cubic inches, the barometer at the time standing at 29·05, the level of the mercury in the gas-vessel being 0·5 inch higher than that outside?

19. What volume would a gas, standing over mercury, measure at the standard pressure, which measures 20 cubic inches, the barometer at the time standing at 28·05, the level of the mercury in the gas-vessel being 1·0 inch higher than that outside?

20. What volume would a gas, standing over mercury, measure at the standard pressure, which measures 15 cubic inches, the barometer at the time standing at 31, the level of the mercury in the gas-vessel being 0·2 inch higher than that outside?

43. *Liquefaction.*—We have seen (5) that when substances are submitted to the action of heat, their temperature is raised, and they increase in volume. These are the first effects of heat on all substances, and they are the only ones produced on gases. But if the application of heat to solids and liquids be continued after these changes have commenced, a temperature is reached at which the solids and liquids change their state. The temperature at which each *solid changes its state, is constant and peculiar to itself, and this is called its melting point, or point of fusion.* A liquid may be regarded as a solid in

combination with a certain amount of heat; this heat, which is necessary for the liquefaction of solids, enters into such intimate combination with *matter*, that it cannot be detected in liquids by the thermometer, or any other means, as long as the matter remains liquefied. It is therefore distinguished from the heat which raises the temperature of substances, and which is, consequently, *sensible*, by the term *insensible*, or *latent* heat.

Example.—A pound of water at 32° F., and a pound of ice at 32° F., indicate by the thermometer the same degree of heat; yet for ice at 32° F. to *pass into* water at 32° F., it must absorb a large quantity of heat, by reason of which it becomes liquefied, and, losing which, the liquid would become solidified. Thus, if 1 lb. of water, at 32° F., be mixed with 1 lb. of water at 174° F., the 2 lbs. of water will have a temperature of 103° F., which is the mean of 32° F. + 174° F.; but if 1 lb. of ice, at 32° F., be mixed with 1 lb. of water, at 174° F., the 2 lbs. of water will only have a temperature of 32° F.; 142° F. degrees of heat have therefore disappeared,—this quantity of heat the 1 lb. of solid (ice), at 32° F., required for its (liquefaction) conversion into water at 32° F.; 142° F. of heat have therefore become latent in the liquefaction of the ice.* This is, therefore, the latent heat of water. We consequently arrive at the following law:—*That when a solid begins to liquefy, it ceases to increase in temperature until the liquefaction is complete, although the heat continues to be applied, because the heat is required for the liquefaction of the solid, and becomes latent.* The facility with which solids liquefy, is proportional to the quantity of the heat they require for their liquefaction. Example:—Ice cannot be liquefied until it has received as much heat as would raise its own weight of water 142° F.; therefore ice liquefies very slowly, because the latent heat of water is considerable; whilst phosphorus and lead are liquefied by as much heat as would raise their own weight of water 9° F.; therefore they melt rapidly, because the heat required for their liquefaction is small.

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* Pouillet has calculated that the whole of the heat of the sun's rays which fall upon the surface of the earth in the course of twelve months, would be expended in melting a layer of ice which covered the entire surface of the globe for a thickness of 104 feet.

44. The amount of heat which is necessary for the conversion of solids into liquids, is disengaged and becomes sensible on the conversion back again of the liquids into solids; in fact, it is on account of the abstraction of this heat that these reconversions take place.

45. *Evaporation* — *Vaporization.* — Solid and fluid bodies, in the gaseous state, are called vapours, and their conversion into this state is called evaporation, or vaporization. Vapours, of which steam is the most familiar to us, are light, expansible, and generally invisible gases, resembling air, and the other permanent gases; but vapours are more readily condensed by a change of temperature than the permanent gases.

46. Vapours, when they are separated from the liquids which have yielded them, obey the same laws (8) as gases; but if the liquid is present, heat not only expands the vapour, but also *increases its volume* by the addition of a new quantity of vapour.

Example.—Steam, when heated by itself, apart from the liquid which produced it, does not possess a greater elasticity than an equal bulk of air confined and heated to the same degree, and may be heated to the temperature at which the containing vessel becomes red hot, without acquiring great elastic force; but if water be present, then more and more steam continues to rise, adding its elastic force to that of the vapour previously existing, so that the pressure becomes excessive.

47. The passage from the liquid state to the state of vapour, *is distinguished from* the passage of the solid state to the liquid state by the important fact that, whilst the liquefaction of each solid is produced *at one* temperature, the vaporization of each fluid occurs at a *variety* of temperatures.

48. When a liquid vaporizes, with or without the application of heat, and the elastic force of the vapour is not equal to the pressure of the atmosphere, the process is called evaporation, and the liquid is said to evaporate.

49. When a liquid vaporizes, with or without the application of heat, and the elastic force of its vapour is equal to the pressure of the atmosphere, the vapour produces a bubbling or boiling, and the liquid is said to boil; and the temperature at which this takes place is called the boiling point of the liquid. In evaporation, the

vapour is formed only from the surface liquid; in boiling, the vapour is formed from the whole mass of the liquid.

50. It will be evident, from what has been stated, that if the pressure of the atmosphere be diminished, either artificially, or by ascending to greater heights in the air, as the tops of lofty mountains, liquids will, on account of the diminished pressure, boil at lower temperatures;* and if the pressure be increased, either artificially, or by descending into mines, liquids will, on account of the increased pressure, boil at higher temperatures; in other words, the boiling point of liquids varies with the pressure. Nevertheless, the temperature at which each liquid boils is quite constant, under the same circumstances, and the boiling point often becomes a physical character of great importance in distinguishing liquids which much resemble each other; as *different* liquids, under the same circumstances, boil at very different temperatures. Ether, for example, boils at 94·8° F., whilst mercury boils, under the same circumstances, at 662° F.

EXAMPLES.

1. The following very simple and beautiful experiment proves that, with the diminution of pressure, liquids boil at lower temperatures. A little water is made to boil in a flask, until all the air is expelled, and the steam issues from the neck. A tightly-fitting cork is then inserted, and the lamp at the same moment withdrawn. By plunging the flask into cold water, the *boiling* is *renewed*, because a partial vacuum is produced by the cold water condensing the steam in the flask. The *boiling ceases* on plunging the flask into hot water, because the steam ceases to be condensed, and its pressure stops the boiling.

2. In a Papin's digester, which is a tight and strong kettle, with a safety valve, water may be raised to 300° F., or 400° F., without boiling, but the instant that this great pressure is removed, the boiling commences with prodigious violence.

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* We have already noticed that the heights of mountains can be measured by means of the barometer; they can also be measured by ascertaining, by means of a very delicate thermometer, at what temperature water boils. A difference of about 1° F. is occasioned by an ascent of about 535 feet.

51. There are other circumstances, besides pressure, which influence the temperature at which liquids boil. The presence of air in a solution has been found to assist the evolution of vapour. Water, deprived of air, may be raised many degrees above its boiling point, and it will then be suddenly converted into steam with explosive violence. "The nature of the vessel, or, rather, the state of its surface, also exercises an influence on the boiling point, and this to a much greater extent than was formerly supposed. It has long been noticed that in a metallic vessel water boils, under the same circumstances of pressure, at a temperature one or two degrees below that at which ebullition takes place in glass; but it has been shown that, by particular management, a much greater difference can be observed. If two similar glass flasks be taken, the one coated in the inside with a film of shellac, and the other completely cleansed by hot sulphuric acid, water heated over a lamp in the first will boil at 211° F., whilst in the second it will often rise to 221° F., or eve higher. A momentary burst of vapour then ensues, and the thermometer sinks a few degrees, after which it rises again. In this state, the introduction of a few metallic filings, or angular fragments of any kind, occasions a lively disengagement of vapour, while the temperature sinks to 212° F., and then remains stationary. These remarkable effects must be attributed to an attraction between the surface of the vessel and the liquid." The solution of solids in a liquid, on account of the adhesion between them, also causes the liquid to boil at a higher temperature.

52. An opinion formerly prevailed that not only bodies which are vaporous at a moderate temperature, but even substances, as the earths, and some of the metals, which cannot be volatilized in the fire, emit vapours at all temperatures, even the lowest. This has been shown by Faraday to be an erroneous opinion. He has proved that there is a temperature below which volatilization ceases; a temperature which varies for different substances. For mercury, the limit is about 40° F.; for sulphuric acid, the limit is much higher, since the acid undergoes no sensible evaporation at ordinary atmospheric temperatures. The cohesive force between the particles of a liquid is greater, probably, than the repel-

lant power between the particles at the temperature at which the liquid ceases to evaporate, and this it is which puts a stop to the evaporation.

53. Some solid bodies, such as camphor and arsenic, pass at once into vapour without being liquefied; but most solids become liquid before they are converted into vapour. Even ice and snow can evaporate without first liquefying. It is owing to this evaporation that patches of snow and tufts of ice are observed gradually to disappear even during the continuance of a severe frost.

54. On the application of heat to a liquid, the temperature of the liquid continues to increase until the boiling point is reached; but the moment ebullition commences, the temperature of the liquid remains stationary, however intense the heat applied may be, and however long continued. "This fact is of importance in domestic economy, particularly in cookery, and attention to it would save much fuel. Soups, &c., made to boil in a gentle way, by the application of a moderate heat, are just as hot as when they are made to boil on a strong fire with the greatest violence."

55. Although liquids are converted into vapours at and below the ordinary temperature of the air, they nevertheless require for this conversion a large amount of heat, which becomes insensible, or latent, in the vapour. If, for instance, a few drops of ether be allowed to fall on the hand, the ether evaporates, and a sensation of cold is experienced, because the ether requires for its vaporization a large amount of heat, which it obtains from the hand, hence the cold. Water may even be frozen by the rapid absorption of heat occasioned by its own evaporation. The porous water-jars which are used in warm countries to keep liquids cool, owe their efficacy to the latent heat of vapours.

56. The sensible heat of vapours is the same as that of the liquids from which they are produced, therefore, a vapour produced from a liquid which has the temperature of 60° F., will also have that temperature; but if the liquid had a temperature of 212° F., the vapour would also have a temperature of 212° F.

57. Equal weights of different liquids require very different amounts of heat to convert them into vapour. But a much larger quantity of heat is necessary to con-

vert fluids into vapours than solids into fluids. As an example, observe the quantity of heat necessary to convert ice into water, and water into steam: 1 lb. of ice at 32° F. requires for its conversion into 1 lb. of water at 32° F., 142° F. of heat; but 1 lb. of water at 212° F. requires for its conversion into 1 lb. of steam at 212° F., 966·6° F.; so that 966·6° F. of heat have disappeared, or become latent, in converting water into the vaporous state; the latent heat of steam is, therefore, 966·6° F.; consequently, the conversion of 1 lb. of steam at 212° F. into water at 212° F. would evolve as much heat as would raise 966·6 lbs. of water 1° F. If the heat necessary for the vaporous state is abstracted, the vapour is converted into the liquid state. The well-known process of distillation is an application of this principle.

58. "We owe to Andrews a careful determination of the latent heat of a number of vapours. Fig. 4 shows the mode of procedure which he adopted. The liquid to be tried is placed in the flask, A, the neck of which has a very short bend, and is connected with a glass receiver, B, furnished with a spiral conducting tube, terminating at *d;* this receiver is placed in a vessel, C, with a considerable quantity of water which has been accurately weighed. The liquid is distilled over into B; the quantity that condenses is carefully weighed, and the rise of temperature experienced by the water used for condensation is estimated by a very sensitive thermometer, *t.* The whole is enclosed in an outer tin-

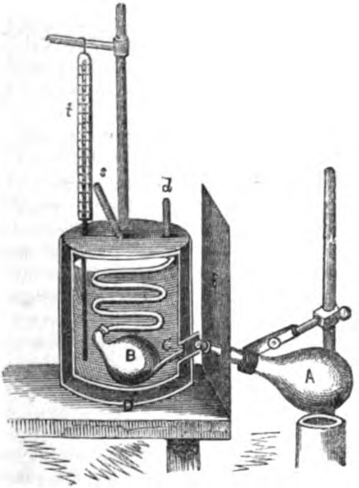

Fig. 4.

plate vessel, D, furnished with a lid, which acts as a screen, and is further protected from the radiation of the lamp by the tin-plate screen, E; *s* is a light glass tube for agitating the water. The result obtained has, however, to be corrected by other experiments, for the heat absorbed by the metallic parts of the apparatus, and for that which is lost by radiation during the time that the experiments last; allowance has also to be made for the heat which the condensed liquid has given out after its liquefaction, in cooling down from its boiling point to the temperature of the water used in the condenser."

Substance.	Equal Weights, ° C.	Equal Weights ° F.	Equal Weights, Steam = 1000	Equal Volumes Steam = 1000.	Boiling Point ° F.	Sp. Gr. at 32° F.
Water . .	536·67	966·6	1000	1000	212·0	1·0000
Wood Spirit	263·70	474·6	491·0	872·9	149·9	0·8179
Alcohol .	202·40	364·3	374·9	963·1	173·1	0·8151
Ether . .	90·45	162·8	168·4	692·3	94·8	0·7365
Oil of Turpentine .	68·73	123·7	128·0	966·9		

59. "The numbers contained in the third column indicate the quantities of water in pounds, the temperature of which would be raised 1°F. by condensation into the liquid form of a pound weight of the vapours of each of the liquids mentioned; the liquid condensed being supposed in each case to be at the temperature of its own boiling point. For instance, the conversion of one pound of steam at 212° into water at 212° would raise 966·6 pounds of water from 60° to 61° F. So the condensation of one pound of the vapour of alcohol at 173° into liquid alcohol at 173° would heat 374·9 pounds of water from 60° to 61°." The numbers in the fourth column are, with the exception of ether, approximatively equal; the same is also true of some other liquids not included in the table; it is, nevertheless, not universally true that equal volumes of vapours of different liquids, under equal pressures, contain equal amounts of latent heat.

60. The heat absorbed in vaporization *decreases* as the temperature of the vaporizing liquid *increases*. For instance, a given weight of water at 212° F. requires less

heat for its vaporization than the same quantity at 100° F. requires, therefore the quantity of heat which is rendered latent by the conversion of a liquid into vapour varies with the temperature at which the evaporation takes place, the quantity of heat which becomes latent increasing as the temperature decreases. Watt concluded from his experiments on steam that liquids require for their conversion into vapour the same total quantity of heat at all temperatures, and as the quantity that remained sensible increased, the quantity that became latent decreased in the same proportion. "For instance:—

A certain weight of steam at 212° F., condensed at 32° F., gives out	180° of sensible heat. 950° of latent heat.
Amounting together to - -	1130°
The same weight of steam at 250°, condensed at 32°, gives out	218° of sensible heat.
But only - - - -	912° of latent heat.
Still amounting together to -	1130°
The same weight of steam at 100°, condensed at 32°, gives out	68° of sensible heat.
But now as much as - -	1062° of latent heat.
Making together, as before -	1130°"[*]

61. If liquids required for their conversion into vapour the same total quantity of heat, there would be no economy in distilling at one temperature rather than another.

62. Regnault has submitted the subject to a rigorous examination, and his results show that the total amount of heat at all temperatures is not the same, but increases by a constant difference equal to 0·305 for each degree C. He found that the latent heat of steam at 0° C. is 606·5; so that the formula for calculating the total quantity of heat in steam at different temperatures becomes—

$$\lambda = 606{\cdot}5 + 0{\cdot}305\,t,$$

in which λ represents the sum of the latent and sensible heat, while 606·5 is the latent heat of the vapour at 0°, and *t* the given temperature.

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[*] Miller's "Chemical Physics," 2nd edit.

63. Equal bulks of different liquids produce very different volumes of vapour. Water furnishes, bulk for bulk, a much larger amount than any other liquid, a cubic inch of water at 212° F. expanding to nearly a cubic foot of steam at 212°, or more accurately, to 1,696 times its volume. The following table shows the volume of vapour which is furnished by a cubic inch of four different liquids, at their respective boiling points. Equal volumes of different vapours, taken at the boiling points of their respective liquids, consequently possess very different weights, as is shown by the last column of the table:—

1 cubic inch of each liquid at 60° F. yields in the case of	Cubic inches of vapour at its boiling point.	Boiling point °F.	Weight in grains of 100 cubic inches of each vapour at its boiling point.
Water .	1,696	212	14·93
Alcohol .	528	173	40·49
Æther . .	298	95	64·71
Oil of Turpentine	193	314	117·71

64. "The expansive force of the different vapours obviously depends upon the bulk of vapour produced from an equal bulk of each liquid; and although the latent heat required to convert equal bulks of other liquids into vapour is much less than that required for steam, yet no economy would be experienced, even did they cost no more than water, by substituting these liquids for water, as the materials for generating vapour in the steam engine." —*Miller*.

65. The elastic force of a vapour varies with the condition under which the vapour is formed; if the vapour is produced below the boiling point of the liquid, its elastic force is not equal to the pressure of the atmosphere (48); if the vapour is produced at the boiling point of the liquid, its elastic force is equal to the pressure of the atmosphere (49); if the vapour is produced above the normal boiling point of the liquid, its elastic force exceeds

the normal pressure of the atmosphere. Steam of greater tension than the atmospheric pressure is called *high pressure* steam. The tension of steam increases very rapidly: at the temperature of 250·52° F. it is equal to two atmospheres (twice the pressure of the atmosphere); at 510·62° F. it is equal to 50 atmospheres.

66. We have now to consider how the tension of vap at different temperatures has been determined.

67. For measuring the elastic force of the vapou water below zero, Gay Lussac made use of two barometer tubes filled with mercury, the open ends dipping under mercury in the same basin. (Fig. 5.) One of the tubes, A, which is straight and perfectly freed from air and moisture, by boiling the mercury in the tube, serves to measure the pressure of the atmosphere. The other tube is bent, so that a part of it can be surrounded with a freezing mixture, as represented in the figure. If we now introduce a few drops of water above the mercurial column in the tube, B C, we observe that the level of the mercury in this tube is lower than in the tube, A, by a quantity which varies with the temperature of the freezing mixture.

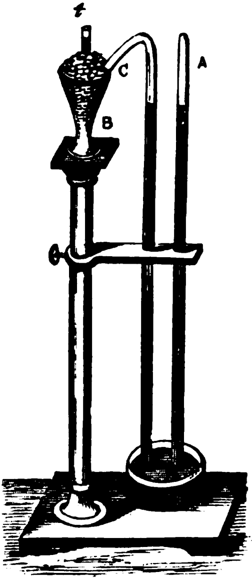

Fig. 5.

0°	C., the depression is in millimetres ...	4·60
—10°	... ...	1·96
—20°	... ...	0·84
—30°	... ...	0·36

These depressions, which are necessarily due to the tension of the vapour in the tube, B C, show that at very low temperatures there is still aqueous vapour in the air.

68. Only a portion of the vapour in the tube, B C, is exposed to the freezing mixture; but it is an established principle of hygrometry, that *when the temperatures of two vessels communicating with each other are unequal, the tension of the vapour is the same in both, and is always that which corresponds to the lowest temperature.*

69. Dalton measured the elastic force of the vapour of water from 32° F. to 212° F. by means of the following apparatus. Two barometer tubes, A and B (Fig. 6), are put into the same basin of mercury, which is placed upon a furnace. The barometer, B, is completely freed from air and moisture; in other words, it is a perfect barometer: the barometer, A, contains a small amount of water above its mercury column. These two barometers are enclosed in a tall glass cylinder filled with water, and a thermometer dips into the water in the centre of the cylinder, which gives the temperature of the liquid. In heating gradually the basin containing the mercury, and consequently the water in the glass cylinder, the water in the tube continues to vaporize, and as the tension of the aqueous vapour augments, the mercury in A falls lower and lower. The depression which is produced in A, below the level in B, for each degree the temperature is increased, is noted upon the scale, E. The apparatus of Dalton can be used so long as the elastic force of the vapour does not exceed the pressure of the atmosphere. When the tension is equal to the atmospheric pressure,

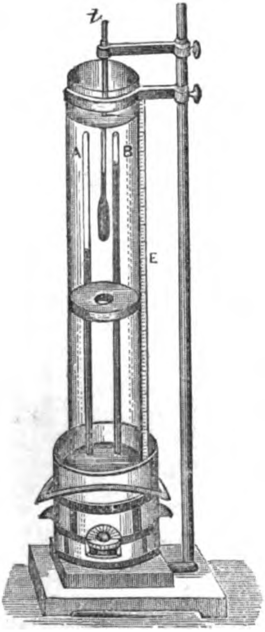

Fig. 6.

the surface of the mercury column will be depressed to the level of the mercury in the basin, and the experiment is at an end.

70. Regnault employed a form of apparatus which has the advantage of indicating all pressures and temperatures, whether above or below the boiling point. "His process consists in boiling water in a vessel under a known pressure, and ascertaining the temperature at which it boils. This method depends upon the principle that when the water boils, the steam it produces will have a pressure precisely equal to that to which the water itself is submitted.

71. "The apparatus consists of a copper boiler (Fig. 7), closed so as to be steam-tight, filled to about a third of its capacity with water, and placed upon a charcoal furnace. The tubes of four thermometers, whose bulbs

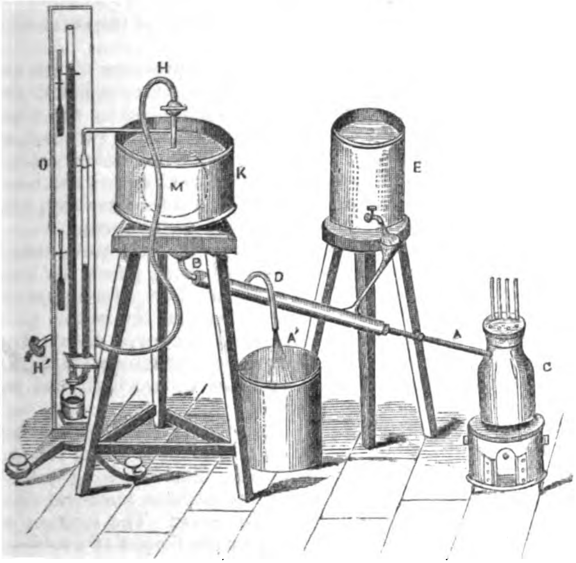

Fig. 7.

descend to different depths in it, pass steam-tight through collars in the top. Two of these bulbs are immersed in the upper, and two others in the lower strata of the liquid. The boiler, C, is connected by a tube, A B, with a large glass globe, M, having a capacity of about five gallons, which is filled with air. The tube, A B, is surrounded by a larger tube, D, which is kept filled with cold water, flowing from a cistern, E, and discharged into another, A′. From the upper part of the globe, M, two tubes proceed, one of which communicates with an air gauge, O, and the other, H, is terminated in a connecting pillar, H′, which may be attached at pleasure, either to the plate of an air pump, or to that of a condenser, so that the air in M can be made to have any degree of pressure, either above or below that of the atmosphere. The globe, M, is immersed in a reservoir of water, at the temperature of the surrounding air.

72. If it be desired to measure the pressure of the vapour of water corresponding to temperatures below the boiling point, the connector, H′, is attached to the plate of an air pump, and the air in M is gradually rarefied, so as to assume a series of decreasing pressures below that of the atmosphere. The thermometer in C, shows the temperatures corresponding to these pressures severally, and the gauge, O, shows the corresponding pressures.

73. If it be desired to ascertain the pressures corresponding to temperatures above the boiling point, the connector, H′, is attached to a condenser or a force pump, by means of which the air in M, and in the boiler, C, is submitted to a series of increasing pressures above that of the atmosphere. The corresponding temperatures, as before, at which the water boils in C, are indicated by the thermometers.—*Lardner.*

74. These researches have resulted in the construction of tables which make known the elastic force of the vapour of water at different temperatures. The following tables give the degree of tension for the various temperatures, at which analyses are likely to be made. The tension of the vapour of water is expressed by the height of a column of mercury counterbalancing it. The first table gives the elastic force in inches of mercury for Fahrenheit's thermometer; the second gives the elastic force in millimetres of mercury for the centigrade thermometer.

TABLE I.—ELASTIC FORCE OF AQUEOUS VAPOUR IN INCHES OF MERCURY, FOR FAHRENHEIT'S THERMOMETER.

Temp. Fah.	Force. Inches of Mercury.	Temp. Fah.	Force. Inches of Mercury.	Temp. Fah.	Force. Inches of Mercury.
0°	0·051	35°	0·208	70°	0·723
1	0·053	36	0·216	71	0·748
2	0·056	37	0·224	72	0·773
3	0·058	38	0·233	73	0·799
4	0·060	39	0·242	74	0·826
5	0·063	40	0·251	75	0·854
6	0·066	41	0·260	76	0·882
7	0·069	42	0·270	77	0·911
8	0·071	43	0·280	78	0·942
9	0·074	44	0·291	79	0·973
10	0·078	45	0·302	80	1·005
11	0·081	46	0·313	81	1·036
12	0·084	47	0·324	82	1·072
13	0·088	48	0·336	83	1·106
14	0·092	49	0·349	84	1·142
15	0·095	50	0·361	85	1·179
16	0·099	51	0·375	86	1·217
17	0·103	52	0·389	87	1·256
18	0·107	53	0·402	88	1·296
19	0·112	54	0·417	89	1·337
20	0·116	55	0·432	90	1·380
21	0·121	56	0·447	91	1·423
22	0·126	57	0·463	92	1·468
23	0·131	58	0·480	93	1·514
24	0·136	59	0·497	94	1·562
25	0·142	60	0·514	95	1·610
26	0·147	61	0·532	96	1·660
27	0·153	62	0·551	97	1·712
28	0·159	63	0·570	98	1·764
29	0·165	64	0·590	99	1·819
30	0·172	65	0·611	100	1·874
31	0·179	66	0·632	101	1·931
32	0·186	67	0·654	102	1·990
33	0·193	68	0·676	103	2·050
34	0·200	69	0·699	104	2·112

TABLE I.—*Continued.*

Temp. Fah.	Force. Inches of Mercury.	Temp. Fah.	Force. Inches of Mercury.	Temp. Fah.	Force. Inches of Mercury.
105°	2·176	112°	2·669	119°	3·257
106	2·241	113	2·747	120	3·349
107	2·307	114	2·826	121	3·444
108	2·376	115	2.908	122	3·542
109	2·447	116	2·992	123	3·641
110	2·519	117	3·078	124	3·743
111	2·593	118	3·166		

TABLE II.—ELASTIC FORCE OF AQUEOUS VAPOUR IN MILLIMETRES OF MERCURY FOR CENTIGRADE THERMOMETER.

Temp. Cent.	Force of the Aqueous Vapour in Millimetres.	Temp. Cent.	Force of the Aqueous Vapour in Millimetres.	Temp. Cent.	Force of the Aqueous Vapour in Millimetres.
0°	4·525	14°	11·882	28°	28·148
1	4·867	15	12·677	29	29·832
2	5·231	16	13·519	30	31·602
3	5·619	17	14·409	31	33·464
4	6·032	18	15·351	32	35·419
5	6·471	19	16·345	33	37·473
6	6·939	20	17·396	34	39·630
7	7·436	21	18·505	35	41·893
8	7·964	22	19·675	36	44·268
9	8·525	23	20·909	37	46·758
10	9·126	24	22·211	38	49·368
11	9·751	25	23·582	39	52·103
12	10·421	26	25·026	40	54·969
13	11·130	27	26·547		

75. The tension of the vapour of other liquids could be determined by the methods which have been given for determining the tension of aqueous vapour.

76. Vapours occupy a much larger volume than the liquids from which they are produced, and equal volumes of different liquids generate very different volumes of vapour. At the same temperature the elastic force of the

vapours of different liquids is different,—the more volatile the liquid the greater the tension of its vapour. This is easily proved for elasticities below that of atmospheric air, by filling a number of barometer tubes (Fig. 8) with mercury, and inverting them in a bath of the same metal. One of the tubes, A, is used as a barometer to measure the pressure of the external air; into B is introduced, by means of a pipette, a few drops of water; into C, a few drops of alcohol; into D, a few drops of bisulphide of carbon; and into E, a few drops of ether: the different liquids will ascend to the top of the mercury and then evaporate. The elastic force of each vapour will depress the column of mercury, but the amount of depression will vary with the liquid; the vapour of water will cause the least depression, and therefore its elastic force is least; alcohol the next; bisulphide carbon the next; and ether the greatest. The elastic force of the vapours counteracts the pressure of the atmosphere to the extent of the depression they cause in the mercurial column, consequently, it is easy to find the pressure each of these vapours exercises, say, upon every square inch; for, if the atmosphere at the time supports a column of mercury 30 inches in length, its pressure is equal to 15 lbs. on every square inch; if the vapour of water depresses the mercurial column one inch, its pressure must be equal to $\frac{1}{30}$ of 15 lbs.; if the alcohol depresses the mercury 2 inches, and the ether depresses it 20, the pressure they exercise is found in the same way. It has been proved that the elasticity of the vapour emitted from each liquid increases as the temperature rises, until, at the boiling point of each liquid, the elasticity of the vapour is equal to the pressure of the atmosphere.

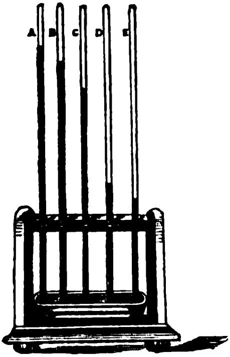

Fig. 8.

77. Dalton considered that all vapours have the same elasticity at an equal number of degrees above or below their boiling points; other experimenters have not found

this to be perfectly correct, although for short distances above or below the boiling point it is very nearly true, except in the case of mercury.

78. The quantity of vapour that can be formed from any liquid depends upon the space and the temperature; the same quantity of vapour will pass into the space if it be filled with gaseous matter or with other vapours, or if it be perfectly empty; the only difference being that it requires a longer time to pass into the space which contains other gaseous or vaporous bodies than it would require if the space were empty. "Different gases and vapours offer no resistance to each other's elasticity; thus, the particles of watery vapour in the air are not subjected to the pressure of the atmosphere, but only influenced by the pressure of the particles of the same kind; and hence, at 32°, when the elasticity of vapour is only 0·200 inch, it retains perfectly its elastic constitution, though diffused through an atmosphere, the elasticity of which may equal thirty inches."

79. The mixture of a gas and vapour obeys the two following laws; these laws were discovered by Dalton, and known under the name of the "Laws of Dalton:"—

1. *The amount of vapour, which will saturate a given space at a given temperature, and its tension are the same, whether the space be completely empty or filled with gas.*

2. *The elastic force of a mixture of gas and vapour is equal to the sum of the tensions which each would have separately.*

80. *Correction of gases for the tension of aqueous vapour.*—We learn from Table I., that the elastic force of the vapour of water at 80° F. would depress the mercurial column one inch; or its tension is one-thirtieth of the usual tension of the air; therefore, if a gas perfectly dry were saturated with aqueous vapour at 80° F., the vapour would increase the tension of the gas, if it were confined, by one-thirtieth; or if the gas were allowed to expand, the vapour would increase its bulk by one-thirtieth. A gas containing aqueous vapour must therefore occupy more space than if it were perfectly dry, by reason of the pressure which the vapour exercises on the confining fluid. It is, therefore, necessary to take care, in measuring gases, that they are either perfectly dry, or thoroughly

saturated with aqueous vapour. To find the actual pressure upon a gas saturated with vapour, we must subtract from the apparent pressure the amount neutralized by the tension of aqueous vapour. Example.—Suppose a gas saturated with aqueous vapour measured 100 cubic inches, the temperature being 50° F., and the atmospheric pressure at the time 29·361 inches; how much space would the gas occupy in the dry state, and at 30 inches pressure? The tension of aqueous vapour at 50° F. is 0·361 (Table I.), therefore, the gas is not under the apparent pressure of 29·361, but under the actual pressure of 29·361 — 0·361 = 29·0 inches; therefore,—

Standard pressure.		Observed pressure.		Observed volume.		True volume.
30	:	29·361 — 0·361 = 29·0	::	100	:	96·6

81. We have to attend to the following points in the measuring of gases:—1. We must determine as accurately as possible the height of the water or mercury in the vessel containing the gas, above that outside; and the difference must be subtracted from the height of the barometric column at the time (42). 2. If moist, we must correct for the tension of aqueous vapour (80). 3. These two corrections being made, and having observed the height of the barometer, we have to subtract from the apparent pressure, the height of the liquid in the gas-vessel and the tension of the vapour, to get the actual pressure to which the gas is subjected at the moment it is measured. 4. We must correct the gas for temperature (12).* As the volumes of gases can be compared only if measured at the same temperature, under the same pressure, and in the same hygroscopic state; the temperature is generally reduced to 60° F.,† the hygroscopic state of the gases to 0, and the pressure to 30 inches.‡

82. If it is desired to find the weight of a gas which has been measured, it is necessary to ascertain the weight corresponding to the volume found, before the proportional amount of the gas in 100 parts by weight of the

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* It does not signify in what order the corrections are made.

† This, as we before stated, is the English standard; the Continental one is 0° C. = 32° F.

‡ The standard pressure adopted on the Continent is 760 millimetres = 29·922 inches.

analysed substance can be calculated. But as the exact weight of a certain definite volume of the various gases has been determined very accurately, the calculation is a simple rule-of-three question, after the gas we have measured has been corrected, if moist, for the tension of the aqueous vapour, and brought to the standard of comparison as regards the temperature and pressure.

83. The following data will be required in some of the exercises:—

1. Hydrogen and oxygen unite in the proportion by measure of two volumes of H to one volume of O.

2. Carbonic oxide and oxygen unite when exploded by the electric spark, 2 volumes of CO combining with 1 volume of O, and forming 2 volumes of CO_2.

3. Absolute weight of atmospheric air and nitrogen, in grammes.

	* One litre (1,000 cubic centimetres) of gas at 0° C. and 760 millimetres barometric pressure.
Atmospheric air - - -	1·29363 grammes.
Nitrogen - - - - -	1·25192 ,,

EXERCISES.

21. If a volume of dry air at 60° F., and under a pressure of 30 inches, measures 80 cubic inches, what will it measure if saturated with water?

22. It has been found by analysis that 100 measures of air contain 79·19 measures of nitrogen and 20·81 measures of oxygen; find the quantity by weight of these substances in 100 parts by weight of air.

23. What is the total quantity of heat in steam at 100° C.?

24. A gas (moist) measured 15 cubic inches, the temperature was 80° F., the pressure was 29·5 inches, and the height of the column of mercury in the vessel containing the gas, above that outside, was 0·25; what volume would the dry gas measure at the English standard for temperature and pressure?

25. A gas (moist) measured 25 cubic inches, the temperature was 45° F., the pressure was 29·0 inches, and the height of the column of mercury in the vessel containing the gas, above that outside, was 0·6; what volume would the dry gas measure at the English standard for temperature and pressure?

26. If air is passed over finely divided copper in a state of ignition, the copper removes the oxygen from the air by combining with it; if 300 cubic inches of air were passed over ignited copper, how much gas would remain unabsorbed by the copper, and how many cubic inches of hydrogen would be required to convert the copper into its metallic state?

27. To a mixture of carbonic oxide and hydrogen, amounting to 35 volumes, 19 volumes of oxygen were added, and the mixture was exploded by the electric spark: after the explosion the gas measured 29 volumes. What were the respective proportions of carbonic oxide and hydrogen in the gaseous mixture?

28. A gas measured over water 15 cubic inches, the temperature was 50° F., the pressure was 29·5 inches, and the height of the column of water, above that in the trough, was 6·8 inches; what would be the measure of the dry gas at the standard (English) pressure and temperature?

29. A gas measured over water 12 cubic inches, the temperature was 70° F., the pressure was 30 inches, and the height of the column of water, above that in the trough, was 10·2 inches; what volume would the dry gas measure at the English standard for temperature and pressure?

30. To 100 volumes of air contained in a eudiometer were added 50 volumes of hydrogen; the gaseous mixture was then exploded: the gas after the explosion measured 87 volumes. Assuming that the 100 volumes were composed entirely of oxygen and nitrogen, what were the respective proportions of each?

31. To 100 volumes of an oxide of nitrogen in the gaseous state were added 150 volumes of hydrogen: after the explosion the gas measured 150 volumes. In order to ascertain the quantity of hydrogen which had combined with the oxygen in the nitrogen compound, 50 volumes of oxygen were added to the 150 volumes of mixed gases, and the mixture was again exploded: after the explosion the gas measured 125 volumes. Find the quantity of hydrogen consumed in the first explosion, and the number of measures of oxygen and nitrogen in 100 measures of the oxide of nitrogen gas, and give the formula of the oxide of nitrogen.

32. A gas (moist) measured 114 millimetres,* the temperature was 16° C., the pressure was 761·4 millimetres, and the height of the column of mercury, above that in the trough, was 72·1 millimetres. Correct the volume for temperature, pressure, and tension of aqueous vapour, giving the corrected volume at 0° C., and 1 metre pressure.

33. A gas (moist) measured 107·9 millimetres, the temperature was 14·3° C., the pressure was 766·8 millimetres, and the height of the column of mercury, above that in the trough, was 59·8 millimetres. Correct the volume for temperature, pressure, and tension of aqueous vapour, giving the corrected volume at 0° C., and 1 metre pressure.

34. A gas (moist) measured 96·8 millimetres, the temperature was 13° C., the pressure was 772·1 millimetres, and the height of the column of mercury, above that in the trough, was 69·6 millimetres. Correct the volume for temperature, pressure, and tension of aqueous vapour, giving the corrected volume at 0° C., and 1 metre pressure.

35. 7·903 grains of a substance gave by Dumas' quantitative method for the estimation of nitrogen 117 cubic centimetres of nitrogen gas, the temperature was 11·1° C., the pressure was 773 millimetres. Correct the volume for temperature, pressure, and tension of aqueous vapour, giving the corrected volume at 0° C., and 760 millimetres pressure; then find what quantity of nitrogen 100 parts by weight of the substance contained.

36. 5·427 grains of a substance gave by Dumas' method 86 cubic centimetres of nitrogen gas, the temperature was 9·4° C., and the pressure was 744 millimetres. Correct the volume for temperature, pressure, and tension of aqueous vapour, giving the corrected volume at 0° C., and 760 millimetres pressure; then find what quantity of nitrogen 100 parts by weight of the substance contained.

37. 4·494 grains of a substance gave by Dumas' method 112 cubic centimetres of nitrogen, the temperature was 8·6° C., the pressure was 758 millimetres. Correct the volume for temperature, pressure, and tension of aqueous vapour, giving the corrected volume at 0° C., and 760 millimetres pressure; then find what quantity of nitrogen 100 parts by weight of the substance contained.

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* A table of French weights and measures will be found at the end of the book.

38. A substance gave by Liebig's* method for the estimation of nitrogen 20·51 volumes of the mixed gases (carbonic acid and nitrogen); after the absorption of the carbonic acid, the gas measured 7·74 volumes: of how many volumes of carbonic acid, and how many volumes of nitrogen, were the 20·51 volumes of the mixed gases composed, and what was the proportion of carbonic acid to nitrogen, taking nitrogen as unity? The substance gave by combustion with chromate of lead 13·288 by weight of carbon in 100 parts; what amount of nitrogen did 100 parts of the substance contain?

39. A substance gave by Liebig's method 21·84 volumes of the mixed gases; after the absorption of the carbonic acid the gas measured 8·4 volumes: of how many volumes of CO_2, and of how many of N, were the 21·84 volumes composed, and what was the proportion of nitrogen to carbonic acid, taking nitrogen as unity? The substance gave by combustion with chromate of lead 21·251 by weight of carbon in 100 parts; what per-centage of nitrogen did the substance contain?

40. The following observations were made in analysing the gaseous mixture of carbonic acid and nitrogen, which an unknown quantity of a substance gave by Bunsen's method for the estimation of nitrogen:—

	Observed volume.	Barometer m. m.	Temperature.	Column mercury.
Volume of mixed gases (moist) -	110·8	757·7	16·2°	217·0
" after absorption of CO_2 (dry)	46·2	761·9	16·2°	218·0

Correct the volume of mixed gases for temperature, pressure, and tension of aqueous vapour, and the gas after absorption for temperature and pressure, giving the corrected volumes at 0° C., and 1 metre pressure; find the proportion of nitrogen to carbonic acid, taking nitrogen as unity; then find the quantity by weight of nitrogen in 100 parts of the substance, the per-centage by weight of carbon being 13·288.

41. The following observations were made in analysing the gaseous mixture of carbonic acid and nitrogen, which an unknown quantity of a substance gave by Bunsen's method for the estimation of nitrogen:—

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* A description of the methods by Bunsen, Dumas, and Liebig, for the estimation of nitrogen, is given in Fresenius' quantitative analysis, and in Greville Williams' work on chemical manipulation.

	Observed volume.	Barometer m. m.	Temperature.	Column mercury.
Volume of mixed gases (moist) -	89·5	761·8	7·0° C.	152·7
„ after absorption of CO_2. (dry)	37·4	762·4	9·2°	205·2

Correct the volumes as in the preceding question, and find the proportion of nitrogen to carbonic acid, taking nitrogen as unity; then find the quantity by weight of nitrogen in 100 parts of the substance, the per-centage by weight of carbon being 24·8.

CHAPTER II.

LAW OF VOLUMES.

Combinations by volume, 84. *Exercises. Monatomic and diatomic gases*, 90. *Exercises. Table of the specific gravities and atomic numbers of the gaseous and vapourizable elements*, 94. *Table of the specific gravities and atomic numbers of the vapours of some of the non-vapourizable elements, calculated from some of their gaseous compounds*, 100. *The different standards adopted for the atomic volumes of substances*, 101. *Exercises. The mode of calculating the atomic measure and specific gravity of substances*, 111. *The views of Berzelius and Gerhardt on volume combinations*, 113. *Density of vapours*, 123. *Gay Lussac's method*, 125. *Dumas' method*, 128. *The application of the specific gravity of vapours*, 131. *Exercises. Buoyancy of the air*, 137. *Weight of a body in air*, 138. *Density of gases, Regnault's method*, 144. *Bunsen's method*, 150. *Exercises. Gas analysis*, 156. *Exercises.*

84. COMBINATIONS BY VOLUME.—We have seen that all gases (and also vapours at some distance above their points of condensation) expand and contract alike, *the pressure being the same*, for equal additions or subtractions of heat (7), and that they also experience the same changes in bulk for equal pressures (20). This uniformity of gases in their relations to heat and pressure, has led some chemical philosophers to believe that in the same volume or bulk all gases contain the same number of ponderable atoms set at equal distances, and whose natural repulsion is expressed by the same law.

85. As it is much easier to measure than to weigh gaseous bodies, it is usual to express their combinations by volume rather than by weight. It is necessary, therefore, to know the specific gravity of gases in order to understand their volume combinations. We shall describe the simplest method for taking the specific gravity of gases, as it is sufficient for our present purpose; we shall afterwards describe other methods which are more difficult of execution, but at the same time more exact.

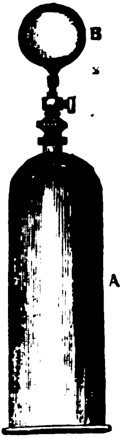

Fig. 9.

86. Fig. 9 represents the apparatus for taking the specific gravity of gases. It consists of a cylinder, A, in which the gas is collected, either over mercury or water; a brass cap with stop-cock is cemented air-tight to the cylinder; a light glass globe, B, is fitted air-tight, with a small brass cap and stop-cock, which screws into the one connected with the cylinder. The operation of taking the sp. gr. of a gas with the apparatus is as follows:—The weight of the globe, when exhausted as perfectly as possible of air by means of the air-pump, is determined; the weight of the globe filled with dry air is then determined, the barometric pressure and temperature, at the time the globe is weighed, being observed: when the sp. gr. of a gas has to be determined, the globe is screwed to an air-pump, and exhausted of air as completely as possible; the exhausted globe is then connected to the cylinder by means of the stop-cocks, which are then opened, and the gas, whose sp. gr. we wish to determine, passes from the cylinder into the empty globe; when the latter is filled with the gas its stop-cock is closed, and it is then weighed, the pressure and temperature being observed. The volume the gas would occupy at the standard temperature and pressure is then calculated, and if the gas be moist, correction must also be made for the tension of aqueous vapour; the way for making these calculations having already been fully explained, we shall not now dwell upon them.

87. If the globe held 46·58 cubic inches of gas at the temperature of 60° F., and under a pressure of 30 inches

of mercury; the weight of the 46·58 cubic inches, at this temperature and pressure, of the different gaseous elements, would be as follows:—

1	Grain of Hydrogen.
14	Grains of Nitrogen.
35·5	„ „ Chlorine.
16	„ „ Oxygen.

Nitrogen is therefore 14 times heavier, and chlorine 35·5 times heavier, than hydrogen; if, therefore, we take hydrogen as the standard for the specific gravity of gases, and represent it by 1, the sp. gr. of nitrogen becomes 14, and the sp. gr. of chlorine 35·5; consequently, the *specific weights* and *atomic weights* of hydrogen, nitrogen, and chlorine are represented by the same numbers: this proves that the *atomic volumes* of these elements are the same; that is to say, that their atoms occupy the same space,—for instance, that an atom of chlorine, or an atom of nitrogen, occupies the same space as an atom of hydrogen, *because the weight of equal volumes of these three gases are as their atomic weights.* But an atom of oxygen can only occupy half the volume which an atom of hydrogen occupies, as oxygen is 16 times heavier than hydrogen; and the oxygen atom is generally considered to be only 8 times heavier than the hydrogen atom, therefore, *in equal volumes* hydrogen and oxygen are in the *proportion by weight* of *two* equivalents of oxygen to *one* of hydrogen. Before entering upon any theoretical discussions, we will give the student a few exercises in order to render these facts familiar to his mind; in performing the exercises, the student must take the *combining measure* of oxygen as *one volume.*

EXERCISES.

42. Nitrogen and oxygen unite in the proportion *by weight* of 14 of the former to 8 of the latter element, to form the gaseous compound NO; in what proportions by volume must they combine?

43. Nitrogen and oxygen unite in the proportion by weight of 14 of the former to 16 of the latter element, to form the gaseous compound NO_2; in what proportions by volume must they combine?

44. Nitrogen and oxygen unite in the proportion by weight of 14 of the former to 24 of the latter element, to form the very volatile liquid NO_3; in what proportions by volume must they combine?

45. In what proportions by volume must nitrogen and hydrogen combine to form NH_3?

46. In what proportions by volume must hydrogen and oxygen combine to form water?

47. In what proportions by volume must hydrogen and chlorine combine to form hydrochloric acid?

48. In what proportions by volume must hydrogen and oxygen combine to form binoxide of hydrogen?

49. In what proportions by volume must chlorine and oxygen combine to form hypochlorous acid ($Cl\,O$)?

88. The weight of 46·58 cubic inches, at the standard temperature and pressure, of the following elements in the state of vapour would be,—

80	Grains of	Bromine.
127	,, ,,	Iodine.
100	,, ,,	Mercury.
32	,, ,,	Sulphur.*
62	,, ,,	Phosphorus.
150	,, ,,	Arsenic.

89. The *specific weight* and *atomic weight* of bromine, of iodine, of mercury, coincide; these elements have therefore the same atomic volume, and the atoms of these elements occupy the same space as the atoms of hydrogen, chlorine, and nitrogen, because the weights of equal volumes of these six elements are as their atomic weights. But as the specific weights of sulphur, of phosphorus, and of arsenic, are, like oxygen, twice that of their atomic weights, the atoms of these elements can only be one-half the size of the atoms of hydrogen, chlorine, &c. We are not speaking of the absolute size of atoms—for this has not been, nor can be, ascertained—but of the relative size of the atoms of these bodies; for instance, whatever may be the size of the hydrogen atoms, the oxygen atoms and the sulphur atoms can only be one-half their size. For if the atoms of these elements were of the same size, these elements would contain in equal volumes the same

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* Until very recently the density of the vapour of sulphur was considered to be 96; hydrogen = 1.

number of atoms, and the relative weights of equal volumes of these gaseous bodies must necessarily coincide or be identical with their atomic weights; as this is not the case, it proves that the atoms of these bodies are not all of the same size. The less the size of the atoms of any substance, the greater the number of the atoms that will occupy a given space; and the greater the weight of these atoms, the greater must be the specific gravity of the substance. For example, two atoms of arsenic or two atoms of oxygen will occupy the same space as one atom of hydrogen, therefore their specific weights must be as follows:—

Arsenic - - - -	150
Oxygen - - -	16
Hydrogen - - -	1

Because two atoms of arsenic occupy the same space as one atom of hydrogen, and the arsenic atom is 75 times heavier than the hydrogen atom, therefore $75 \times 2 = 150$; and two atoms of oxygen occupy the same space as one atom of hydrogen, and the oxygen atom is 8 times heavier than the hydrogen atom, therefore $8 \times 2 = 16$. Hence the specific gravity is obtained by multiplying the atomic number by the atomic weight; and the specific gravity divided by the atomic weight gives the *atomic number*, that is to say, the *number of atoms in a given volume.*

90. The gaseous and vapourizable elements may be divided into the two following classes:—

1st. *Monatomic gases.* Hydrogen, chlorine, nitrogen, iodine, bromine, and mercury.

2nd. *Diatomic gases.* Oxygen, sulphur,* arsenic, phosphorus.

91. This division the student will readily understand; by the terms monatomic and diatomic are meant, that one atom of a monatomic gas, and two atoms of a diatomic gas, occupy a given volume. Therefore, in order to bring together two gaseous or vapourizable bodies in equal number of atoms, equal volumes of the bodies must be taken, if they belong to the same class; but if one of them belongs to the diatomic class, and the other to the monatomic class, then, in order to bring them together in *equal*

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* Before the recent determination of the density, the vapour of sulphur was regarded as a hexatomic gas.

number of atoms, they must be brought together in the proportion, by volume, of 1 of the diatomic to 2 of the monatomic body.

92. In the following exercises, which the student must now write out, the *combining measure* of hydrogen must be taken as *one volume*.

EXERCISES.

50. In what proportions by volume must hydrogen and sulphur combine, to form sulphide of hydrogen?

51. In what proportions by volume must hydrogen and bromine combine, to form bromide of hydrogen?

52. In what proportions by volume must sulphur and oxygen combine, to form sulphurous acid?

53. In what proportions by volume must phosphorus and hydrogen combine, to form $P\,H_3$?

54. In what proportions by volume must sulphur and oxygen combine, to form $S\,O_3$?

55. In what proportions by volume must chlorine and phosphorus combine, to form terchloride of phosphorus?

93. The student will not have failed to notice, in obtaining answers to the last two series of exercises, that gaseous substances unite by volume* in the simple ratio of 1 to 1, 1 to 2, 1 to 3. It thus appears that the laws of combination may be deduced as well from their volume combinations,† as from their combinations by weight.

94. In the following table is a list of the simple bodies which are naturally gaseous, and those which can be converted into gases by heat.

In column A, the names of the elements are given.

In column B, their atomic weights.

In column C, their specific gravities, hydrogen being taken as unity.

In column D, their atomic numbers, obtained by dividing their specific gravities by their atomic weights.

In column E, their specific gravities, air being taken as unity.

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* On every occasion when volumes are spoken of in chemistry without any further explanation, the student must understand volumes of the substances in the state of gas.

† Gay Lussac was the discoverer of the laws of volume combination, which he made known shortly after the announcement of the atomic theory by Dalton.

In column F, their atomic numbers, obtained by dividing their atomic weights by their specific gravities, air being taken as 1.

In column G, the atomic numbers in F, reduced to their simplest expression.

A	B Atomic weights.	C Sp. gr. Hydrogen=1.	D Atomic numbers.	E Sp. gr. Air=1.	F Atomic numbers.	G Atomic numbers reduced.
Hydrogen	1	1	1	0·0693	14·43	1
Nitrogen...	14	14	1	0·9706	14·43	1
Chlorine ...	35·5	35·5	1	2·4543	14·43	1
Oxygen ...	8	16	2	1·1093	7·23	½
Vapour						
Of Iodine..	127	127	1	8·716	14·43	1
,, Bromine	80	80	1	5·540	14·43	1
,, Mercury	100	100	1	7·000	14·43	1
,, Phosphorus......	31	64	2	4·420	7·23	½
,, Arsenic..	75	150	2	10·600	14·43	½
,, Sulphur*	16	31·705	2	2·23	7·17	½

95. The reason we have given in the table two standards, hydrogen and air, for the specific gravity of gases, is this;—it is the custom to compare the density of gases with that of air, but as air is not either a simple body, or a chemical compound, it does not show the relations subsisting between the specific gravities and atomic weights of gases, but if hydrogen is taken as a standard, these relations are at once perceived.

96. We have seen, in studying combinations by weight, that the atomic weight of a compound is equal to the sum of the atomic weights of the elements composing it.† *But the measure or volume of a compound gas is not always equal to the sum of the measures or volumes of the elementary gases which compose it, contraction or condensation frequently takes place.* When equal volumes of elementary gases combine, the volume of the compound gas is either the sum of the volumes of its constituents, or

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* The recent determination of the density of the vapour of sulphur was made at a much higher temperature (the boiling points of cadmium and zinc) than the former ones; the density according to the former determinations was 6·9. Air = 1.

† See the author's "First Step in Chemistry," page 72, 3rd edition.

is half that sum. When two volumes of one elementary gas combine with one volume of another elementary gas, the resulting gaseous compound usually occupies two volumes. Owing to this uncertainty in the condensation of the combining gases, we cannot find by calculation the density of one of the elements of a compound, from the density of the other element and the density of the compound; we require also to know the contraction of the two elements at the time of their combination. For example, to calculate the density of oxygen from water, we must not only know the density of hydrogen and the density of water, but we must also know the contraction of the hydrogen and oxygen at the time of their combination, thus :—

2 volumes of vapour of water	$0{\cdot}622 \times 2 = 1{\cdot}244$
Less 2 volumes of hydrogen . . .	$0{\cdot}069 \times 2 = 0{\cdot}138$
	$1{\cdot}106$

97. Several of the elements, which cannot be vapourized in their uncombined state, form by their union with other elements compounds which are either gaseous, or which are capable of being converted into vapour. The density of the vapour of these non-vapourizable elements, must therefore be *hypothetical,* because we have seen that in order to *calculate* the density of the vapour of a simple body, we must know not only the density of the compound formed, but also the amount of contraction (if any) which takes place between the elements at the time of their combination, which is impossible in the case of a non-vapourizable element; the density, therefore, of the vapour of a non-vapourizable element can only be *inferred* from the density of its compounds.

Example.—If a piece of charcoal is burned in oxygen gas, so as to convert the whole of the oxygen into carbonic acid, when the combustion is finished, and the gas has returned to its original temperature, it will be found that the volume of the gas has not sensibly changed; we hence conclude that carbonic acid contains a volume of oxygen equal to itself. One volume of carbonic oxide requires for its conversion into carbonic acid half a volume of oxygen, and the carbonic acid produced from this quantity of carbonic oxide and oxygen, is one volume, consequently carbonic oxide contains only half a volume of oxygen. Now if we suppose carbonic acid to be composed of equal volumes of carbon-vapour and oxygen condensed to one-half, carbonic oxide will consist of two volumes of carbon-vapour and one volume of oxygen, the three volumes condensed into two. On this supposition, the density of the vapour of carbon will be 0·4183, as shown by the following calculation:—

Weight of 1 volume of carbonic acid . .	1·5240
Weight of 1 volume of oxygen	1·1057
	0·4183

98. But if we suppose carbonic acid to be composed of two volumes of oxygen and one volume of the vapour of carbon, the three volumes condensed into two, carbonic oxide will, on this supposition, consist of equal volumes of its two elements united without condensation. On this hypothesis, the density of the vapour of carbon will be 0·8366, as shown by the following calculation:—

Weight of 2 volumes of carbonic acid	1·5240×2=3·0480
Weight of 2 volumes of oxygen . .	1·1057×2=2·2114
	0·8366

99. It does not necessarily follow that the true specific gravity of carbon-vapour is either of these numbers; all that can be safely said is, that should the true specific gravity of carbon-vapour ever be determined, it will be found to coincide with the number 0·4183, or it will be double that number, viz., 0.8366, or it will bear some other simple and obvious relation to it.

100. The hypothetical density of the vapour of the following non-vapourizable elements is calculated from the density of the gaseous or vapourizable compounds of which they are components.

In column A, the names of the elements are given.

In column B, their atomic weights.

In column C, their specific gravities, hydrogen being taken as unity.

In column D, their atomic numbers, obtained by dividing their specific gravities by their atomic weights.

In column E, their specific gravities, air being taken as unity.

In column F, their atomic numbers, obtained by dividing their atomic weights by their specific gravities, air being taken as 1.

In column G, the atomic numbers in F, reduced to their simplest expression.

A Vapour.	B Atomic weights.	C Sp. gr. Hydrogen=1.	D Atomic numbers.	E Sp. gr. Air=1.	F Atomic numbers.	G Atomic numbers reduced.
Of Carbon..	6	6·0	1	0·4183	14·43	1
„ Boron ...	10·9	23·0	2	1·50639	7·23	½
„ Selenium	39·5	78·3	2	5·43076	7·27	½
„ Tellurium	64·2	128·6	2	8·91674	7·20	½
„ Fluorine.	19·0	19·0	1	1·32673	14·32	1
„ Silicon ...	21·3	42·5	2	2·94369	7·23	½
„ Antimony	120·3	236·3	2	16·3800	7·34	½

101. *The atomic or equivalent volume of a substance is the quotient obtained by dividing the atomic weight of the substance by its specific gravity.* As the atomic volume is not an absolute quantity, but only expresses the relation by volume in which substances combine, it follows that different but relative expressions will be obtained according as the equivalents are based on the oxygen or hydrogen scale; different expressions will also be obtained according to the standard we employ for the specific gravities; only the atomic volumes of those substances are comparable whose specific gravities are referred to the same standard. If we take the volume which one grain (one atom) of hydrogen occupies at the standard temperature and pressure, as the standard, in that case the combining measure of hydrogen and the other bodies we have termed monatomic becomes one volume, whilst the combining measure of oxygen and the other bodies we have termed diatomic becomes half a volume. If, on the other hand, we take the volume which 8 grs. (one atom) of oxygen occupies as the standard,

in that case the combining measure of the bodies we have termed diatomic becomes one volume, and the combining measure of the bodies we have termed monatomic becomes two volumes, because the atoms of the latter class occupy double the space the atoms of the diatomic bodies occupy. As the specific gravity of oxygen is 16 times greater than that of hydrogen, if we take 8 as the specific gravity of oxygen and make that the standard, the specific gravity of hydrogen becomes 0·5, and accordingly the combining measure of oxygen becomes one volume, and the combining measure of hydrogen (and the other gases we have termed monatomic) becomes two volumes, because—

$$\frac{8}{8} = 1 \text{ volume, and } \frac{1}{0{\cdot}5} = 2 \text{ volumes.}$$

102. But if we take the specific gravity of hydrogen as 1, and make that the standard, then the specific gravity of oxygen becomes 16, and accordingly the combining measure of hydrogen becomes one volume and the combining measure of oxygen becomes half a volume, because—

$$\frac{8}{16} = 0{\cdot}5 \text{ volume, and } \frac{1}{1} = 1 \text{ volume.}$$

103. If we take air as the standard for the specific gravities, which is the one most frequently adopted, the specific gravity of oxygen by this standard is 1·1093, and the specific gravity of hydrogen is 0·0693; now if we divide the atomic weights of these elements by these numbers we obtain as quotients 7·22 and 14·44; thus,—

$$\frac{8}{1{\cdot}1093} = 7{\cdot}22 \qquad \frac{1}{{\cdot}0693} = 14{\cdot}44.$$

According to the standard we adopt, viz., whether the combining measure of hydrogen is one volume or two volumes, so the 14·22 represents one or two volumes, and in the same way the 7·22 for oxygen represents half a volume or one volume.

104. As it is necessary for the perfect knowledge of volume combinations that the student should fully under-

stand this part of the subject, we will illustrate it still further by taking a compound body as an example; the compound body shall be the well-known one, hydrochloric acid. If we take the combining measure of hydrogen as one volume, that is to say, that whatever that measure may be, it is the space which 1 grain of hydrogen occupies at a given temperature and pressure, then the hydrogen and chlorine will combine to form hydrochloric acid in the following proportions by volume:—

1 volume of hydrogen	1·0
1 „ chlorine	35·5
Weight of 2 volumes of hydrochloric acid	36·5

The specific gravity of hydrochloric acid is 18·25 (hydrogen = 1), which is the weight of one volume of hydrochloric acid, that is, the measure which 1 grain (one atom) of hydrogen occupies; therefore an atom of hydrochloric acid occupies two volumes. The atomic measure of hydrochloric acid gas is therefore the sum of the atomic measures of its elements; there is no condensation. But if we make the combining measure of oxygen to be one volume, then the combining measure of hydrogen and similar gases becomes two volumes; in this case the weight of one volume of any of the gases we have termed monatomic is only half that of its atomic weight, accordingly hydrogen and chlorine will combine to form hydrochloric acid, in the following proportions by volume:—

2 volumes of hydrogen	1·0
2 „ chlorine	35·5
Weight of 4 volumes of hydrochloric acid	36·5

The specific gravity of hydrochloric acid is 9·12 (oxygen = 8), which is the weight of one volume of hydrochloric acid gas, that is, a measure which 1 atom or 8 parts by weight of oxygen, or half an atom or 0·5 parts by weight of hydrogen occupies; therefore an atom of hydrochloric acid gas by this standard occupies four volumes, which is the sum of the atomic measure of its constituents.

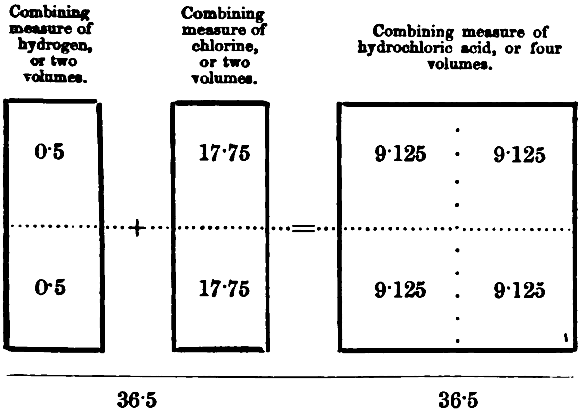
105. The specific gravity of hydrochloric acid is 1·269 (air = 1), therefore $\frac{36·5}{1·269} = 28·70$. Now 28·70 corresponds to two or four volumes just as we assume that 7·22 represents half or one volume of oxygen. If we adopt the first hypothesis, the combining measure of hydrogen and similar gases is one volume; if, on the other hand, we adopt the second hypothesis, in that case the combining measure of hydrogen and similar gases is two volumes.

106. There is an expression frequently made use of in chemical writings, the explanation of which the student will now be able to understand; it is that the compound forms four volumes of vapour, or that the elements form by their combination four volumes of the compound gas, or, as it is frequently stated, they are condensed to four volumes. The meaning of this is, that a substance whose atomic volume in the gaseous or vapourous state is equal to that of oxygen, or is two or four times as great, is said to exhibit a condensation to one, two, or four volumes: almost, if not all organic compounds, exhibit a condensation to four volumes. If, however, we take the combining measure of hydrogen to be one volume, the four volume gas or vapour, by the oxygen standard, is according to the hydrogen standard a two volume gas or vapour. The reason of this difference we have fully explained, but we will restate it very briefly; it is due to the difference in the standard adopted; by the one standard, the combining measure which contains one atom of oxygen is one volume, and the combining measure of hydrogen which contains one atom is two volumes; by the other standard, the combining measure which contains one atom of hydrogen is one volume, and the combining measure which contains one atom of oxygen is half a volume.

107. The atomic measure of the combining gases, and the number of volumes the compound formed occupies, is usually expressed in chemical writings by means of small squares: Mr. Griffin expresses them by means of vulgar fractions; he represents the sum of the atomic measures of the constituents by the *denominator*, and the number of resulting volumes by the *numerator:* this plan is much to be preferred, in my opinion.

108. By the old plan, the combining measure of hydro-

chloric acid and its constituents would be represented thus :[*]—


Combining measure of hydrogen, or two volumes.
Combining measure of chlorine, or two volumes.
Combining measure of hydrochloric acid, or four volumes.
0·5
0·5
+
17·75
17·75
=
9·125
9·125
9·125
9·125
36·5
36·5

109. By Mr. Griffin's plan thus :—

Atomic measure of hydrochloric acid $= \frac{4}{4}$

110. The following exercises must now be performed by the student :—

EXERCISES.

56. In what proportions by volume do hydrogen and nitrogen combine to form gaseous ammonia (NH_3), the combining measure of oxygen being taken as one volume; and what is the atomic measure of ammonia, its sp. gr. being 0·5967 (air = 1)? State whether there is any condensation.

57. In what proportions by volume do carbon-vapour and hydrogen combine to form carburetted hydrogen gas ($C_2 H_4$), the combining measure of hydrogen being taken as one volume; and what is the atomic measure of this

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[*] The *dotted* lines are for the purpose of showing that the division is imaginary, the partition of the combining measure, like that of an atom which it represents, being impossible.

compound, its sp. gr. being 0·5596 (air = 1)? State whether there is any condensation.

58. In what proportions by volume do carbon-vapour and hydrogen combine to form olefiant gas ($C_4 H_4$), the combining measure of hydrogen being taken as one volume; and what is the atomic measure of olefiant gas, its sp. gr. being 0·9852 (air = 1)? State whether there is any condensation.

59. In what proportions by volume do carbon-vapour and oxygen combine to form carbonic acid gas, the combining measure of oxygen being taken as one volume; and what is the atomic measure of the compound, its sp. gr. being 1·524 (air = 1)? State whether there is any condensation.

60. In what proportions by volume do carbon-vapour, oxygen, and chlorine combine to form chloro-carbonic acid gas (CO Cl), the combining measure of oxygen being taken as one volume; and what is the atomic measure of the compound, its sp. gr. being 3·399 (air = 1)? State whether there is any condensation.

61. In what proportions by volume do carbon-vapour, oxygen, and hydrogen combine to form ether ($C_4 H_5 O$), the combining measure of oxygen being taken as one volume; and what is the atomic measure of the compound, its sp. gr. being 2·586 (air = 1)? State whether there is any condensation.

62. In what proportions by volume do carbon-vapour, oxygen, and hydrogen combine to form alcohol ($C_4 H_5 O, HO$), the combining measure of oxygen being taken as one volume; and what is the atomic measure of the compound, its sp. gr. being 1·613 (air =1)? State whether there is any condensation.

63. In what proportions by volume do carbon-vapour, oxygen, and hydrogen combine to form acetic acid ($C_4 H_3 O_3 HO$), the combining measure of oxygen being taken as one volume; and what is the atomic measure of the compound, its sp. gr. being 2·08 (air = 1)? State whether there is any condensation.

64. In what proportions by volume do ammonia ($N H_3$) and sulphide of hydrogen combine to form sulphide of ammonium, the combining measure of hydrogen being taken as one volume; and what is the atomic measure of sulphide of ammonium? The sp. gr. of ammonia

is 0·5967, sulphide of hydrogen 1·1786, and sulphide of ammonium 0·785 (air = 1).

111. The student will not have failed to observe, in performing the last series of exercises, that if, of the atomic weight, the atomic measure, and the specific gravity of a gas, we know two terms, it is easy to find the third:—

Let *a. m.* = Atomic measure.
a. w. = Atomic weight.
sp. gr. = Specific gravity.

We have seen that the atomic measure is the quotient obtained by dividing the atomic weight by the specific gravity:—

$$\frac{a.\ w.}{sp.\ gr.} = a.\ m.$$

The specific gravity must therefore be the quotient obtained by dividing the atomic weight by the atomic measure:—

$$\frac{a.\ w.}{a.\ m.} = sp.\ gr.$$

And the atomic weight must be the product obtained by multiplying the specific gravity by the atomic measure:—

$$sp.\ gr. \times a.\ m. = a.\ w.$$

112. The student ought to prove the truth of the last two rules by the last series of exercises.

113. We must now direct the attention of the student to the views of Berzelius and Gerhardt, especially those of the latter. These distinguished chemical philosophers assume *that all elementary gases contain in the same volume or bulk, under like conditions of temperature and pressure, the same number of atoms* (84). If this hypothesis be adopted, the *atomic and volume constitution of compounds will correspond;* but it will necessitate, of course, a change in the atomic weights of some of the elementary bodies.

114. The atomic weights in the system of Berzelius are the same as those at present in use, with the exception of those of HYDROGEN, NITROGEN, PHOSPHORUS, CHLORINE, BROMINE, IODINE, and FLUORINE, which are

halved. The symbol for water by this system is H_2O, because it is composed of two volumes (two atoms) of hydrogen, and one volume (one atom) of oxygen, consequently the atomic and volume constitution correspond.

115. Gerhardt has carried out the system more fully; if the atomic weight of oxygen equal 8 in Gerhardt's notation, all the other elements, with the exception of sulphur, selenium, tellurium, and carbon, have only half the usual values; but it is more general, and more convenient, to assume that the atom of hydrogen equals 1, then the atomic weights of OXYGEN, SULPHUR, SELENIUM, TELLURIUM, and CARBON become doubled, whilst the atomic weights of the other elements remain as at present. Whichever standard, hydrogen or oxygen, is adopted for the atomic weights, if we adopt the same standard for the specific gravities, the specific gravities of the gaseous and vapourizable elements represent their atomic weights, with the exception of phosphorus and arsenic, whose specific gravities are double their atomic weights. The following table is given to illustrate these statements:—

Name of Element.	New Equivalent.	Specific gravity. Hydrogen=1.
Hydrogen.........	1	1
Oxygen............	16	16
Sulphur	32	31·705
Chlorine	35·5	35·5
Bromine	80	80
Iodine	127	127
Nitrogen	14	14
Phosphorus	32	64
Arsenic............	75	150
Mercury	100	100

116. Compounds expressed by Gerhardt's system also exhibit a like constancy of relation between their atomic weights and specific gravities; the specific gravity of the compounds in the state of gas or vapour is half that of their atomic weights; the atomic measure of compounds by this system is therefore two volumes. "The relation between

the atomic weight and specific gravity in the state of vapour has been so uniformly observed, that chemists are inclined to doubt the exactitude of the formula of all compounds, the atomic weight of which does not yield two volumes of vapour, and the determination of the vapour-density of a compound has thus become one of the most important means of controlling chemical formulæ." To illustrate this relation between the specific gravities and atomic weights of compounds, we will select three compounds which are distinguished from each other by difference in the volume and atomic proportions of their elements, and by the condensation which accompanies the combination; yet these compounds, although so different in these respects, all correspond to two volumes—the compounds are hydrochloric acid, water, and ammonia.

117. Hydrochloric acid, which is the type of the chlorides, bromides, iodides, fluorides, and cyanides, is composed of one volume of each of its elements; the combination is not attended with condensation; the atomic measure of the gas is therefore two volumes. Consequently the sp. gr. must be half that of the atomic weight; see 1st example, par. 104, page 53.

118. Water ($H_2\Theta$), which is the type of the oxides, sulphides, selenides, and tellurides, is composed of two volumes of H, and one volume of O, the three volumes being condensed into two; its atomic measure is consequently two volumes, and the sp. gr. of the vapour is only half that of the atomic weight.

Symbol.		Sp. gr. H=1.	Atomic weight.	Volume.
H_2	=	2	2	2
Θ	=	16	16	1
$H_2\Theta$	=	9	18	2

119. Ammonia (NH_3), which is the type of the nitrides, phosphides, arsenides, and antimonides, is composed of three volumes of H, and one volume of N, the four volumes being condensed into two; its atomic measure is consequently two volumes, and its sp. gr. is only half that of its atomic weight.

Symbol.		Sp. gr. H = 1.	Atomic weight.	Volume.
H_3	=	3	3	3
N	=	14	14	1
H_3N	=	8·5	17	2

120. According to Gerhardt's notation, then, the sp. gr. of compounds in the gaseous or vapourous state is only half that of their atomic weights; in other words, the atom of the compound in the gaseous state occupies two volumes; but the sp. gr. and atomic weight of the elementary bodies correspond, consequently the atomic weights of these bodies *only* represent *one* volume of vapour; Gerhardt proposes to alter this, and bring both classes of bodies, compounds and elements, under the same standard. It will be shown in a following chapter that it is highly probable—indeed, Mr. Brodie has almost proved it experimentally—that the atoms of the elementary bodies in their free state are double what they are when combined with other bodies; for example, the symbol for hydrogen in the free state is not H, but H H, and so with all the other elements. The atoms of the elements in the free state are therefore not considered to exist detached, but to be united in pairs; consequently, on this hypothesis, an elementary body, when it is liberated from its combination with other bodies, must combine with itself, and the atoms of the body must separate in pairs; also, when it enters into combination with another element, double decomposition must ensue, for example:—

$$\mathrm{HH} + \mathrm{Cl\,Cl} = \mathrm{H\,Cl} + \mathrm{H\,Cl} = 2 \text{ atoms } \mathrm{H\,Cl}.$$

Gerhardt has adopted this hypothesis, and he distinguishes between the smallest quantities in which an element is capable of entering into combination with other bodies, and the smallest quantity of an element which is supposed to be capable of existing in the free state; the first is termed the elementary atom, the latter the molecular atom.

121. The molecular atoms of the elements, possessing, as they do, the double weight of the elementary atoms, correspond, with the exception of phosphorus and arsenic,

to two volumes of gas or vapour, as is shown in the following table:*—

Name of element.	Specific gravity.	Atomic weight.		Atomic volume.	Molecular weight.		Molecular volume.
Hydrogen	1	H	1	1	HH	2	2
Oxygen ..	16	~~O~~	16	1	~~OO~~	32	2
Sulphur ...	32	~~S~~	32	1	~~SS~~	64	2
Chlorine ...	35·5	Cl	35·5	1	ClCl	71	2
Bromine ...	80	Br	80	1	BrBr	160	2
Iodine	127	I	127	1	II	254	2
Nitrogen...	14	N	14	1	NN	28	2
Phosphorus	62	P	31	½	PP	62	1
Arsenic ...	150	As	75	½	AsAs	150	1
Mercury ...	100	Hg	100	1	HgHg	200	2

122. The organic radicals, as methyl, ethyl, butyl, &c., and other organic bodies, on the old view represent only *one* volume of vapour, their atomic weights and specific gravities corresponding, but in the next chapter we shall see that there are even more cogent reasons for doubling the atoms of these bodies in their free state than for doubling the atoms of the elementary bodies; and if the atoms are doubled, then the sp. gr. is only half that of their atomic weights; consequently, the atomic measure of these bodies becomes two volumes.

123. DENSITY OF VAPOURS.—The density of a vapour is the ratio between the weight of a certain volume of the vapour and that of the same volume of atmospheric air, under the same conditions of temperature and pressure. We have therefore to ascertain the weight, p', of a volume of air, v, at the temperature t, and under the pressure H_o; now at 0° C., and at the standard pressure (760 m.m.) 1 cubic centimetre of air weighs 0·001293 grammes, therefore the weight of the volume, v, at the same temperature and pressure, will be arrived at by the following calculation, $0{\cdot}001293 \times v$. The co-efficient of the expansion of air, 0·003665, being represented by a, it is evident that

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* The tables illustrating Gerhardt's system have been taken from the eighth edition of Fownes' "Chemistry."

the *volume* of air *will increase* from 0° C. to t degrees, in the proportion of 1 to $1 + at$; the *weight*, on the contrary, for equal volumes *will decrease* in the proportion of $1 + at$ to 1; therefore the weight of the volume of air, v, at t degrees, and at the standard pressure, will be obtained by the following formula:—

$$\frac{0{\cdot}001293 \times v}{1 + at}$$

Consequently, to arrive at the weight of a like volume at the pressure H_0, we must multiply the quantity $\frac{0{\cdot}001293 \times v}{1 + at}$ by $\frac{H_0}{760}$ which gives $\frac{0{\cdot}001293 \times v \times H_0}{(1 + at) \times 760}$ for the weight, p', of a volume of air, v, at the pressure H_0, and at t degrees.

124. Two different methods are used for determining the density of vapours: in the first, which was invented by Gay Lussac, the volume occupied by a known weight, p, of the volatile substance, at the temperature t, and under the pressure $H - h$, is measured; whilst in the second method, which was invented by Dumas, the substance is vapourized in a flask, of which the volume has been previously determined, and the weight of vapour which fills it is determined by experiment.

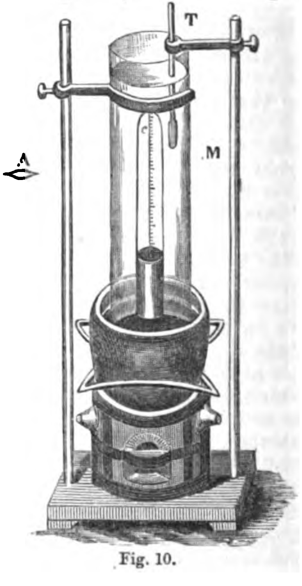

Fig. 10.

125. *Gay Lussac's method.*—The apparatus, Fig. 10, consists of an iron pot filled with mercury, into which is placed a cylinder of glass, M, open at both ends; this cylinder is filled with water, unless it is requisite to observe the volume of vapour at a temperature above 100° C., in that case a fixed oil,

which should be as colourless and transparent as possible, is used in place of water. The temperature is indicated by the thermometer, T. Inside the cylinder is a graduated glass jar, C, filled with mercury, and inverted in the iron pot. In using this apparatus, the liquid to be vapourized is placed in a very thin glass bulb, A, which is then hermetically sealed; the weight of the liquid employed is ascertained by weighing the bulb both before and after it has been filled. The bulb is then passed up into the graduated glass jar, C, and the glass cylinder, M, is then placed over the graduated jar, and is filled with water or oil; the apparatus, thus arranged, is placed on a charcoal furnace. The thin glass bulb containing the liquid rises to the top of the graduated glass jar, C; the heat is gradually applied, until the water or oil in the cylinder reaches a few degrees above that at which the liquid in the bulb begins to boil; the bulb bursts by reason of the expansion of the liquid, which after it escapes from the bulb, becomes converted into vapour, and consequently causes the mercury in the graduated jar to fall as shown in Fig. 10. The mercury must always stand a little higher inside than outside the graduated tube, as this shows that all the liquid has been converted into vapour, which of course is necessary. The volume of the vapour is then ascertained by means of the graduated scale on the glass jar, C, its temperature is indicated by the thermometer, T, and the pressure to which it is subjected is equal to the height of the barometer less the height of the mercury remaining in the jar. There remains then only to ascertain the weight of an equal volume of air under the same conditions of temperature and pressure, and then to divide the weight of the vapour by that of the air; the quotient will be the density or specific weight required.

126. Let p represent the weight of the vapour in grammes; v its volume in cubic centimetres, t its temperature, H the height of the barometer, and h the height of the mercury in the graduated jar. It is required to ascertain the weight, p', of a volume of air, v, at the temperature, t, and under the pressure $H - h$; and let a represent the co-efficient of the expansion of air. The density can be calculated by means of the following equation:—

$$D = \frac{p}{p'} = \frac{p\,(1 + a\,t)\,760 \text{ m.m.}}{\cdot 001293\, v\, (H - h).}$$

127. This method is not well adapted for temperatures above 150° C., or 170° C.; but Dumas' method is applicable to any temperature.

128. *Dumas' method.*—The following is a sketch of the plan of operation by this method:—A light glass globe, *a* (Fig. 11), about three inches in diameter, is taken, and its neck softened and drawn out in the blowpipe-flame as represented; after it is accurately weighed, about one hundred grains of the volatile liquid are then introduced, by gently warming the globe and dipping the point into the liquid, which is then forced upwards by the pressure of the air as the vessel cools. The globe is then firmly attached by wire to a handle, *b* (Fig. 11), in such a manner that it may be plunged into a bath of boiling water or heated oil (Fig. 12), and steadily held with the point projecting upwards. The bath must have a temperature considerably above that of the boiling point of the liquid; the latter becomes rapidly converted into vapour, which escapes by the narrow orifice, chasing before it the air in the globe. When the issue of vapour has wholly ceased, and the temperature of the bath, carefully observed, appears fully uniform, the open extremity of the point is hermetically sealed by a small blowpipe-flame. The globe is removed from the bath; when cold it is cleansed, if necessary, and then weighed,

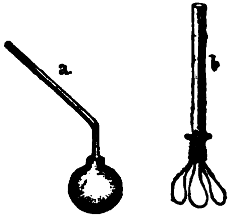

Fig. 11.

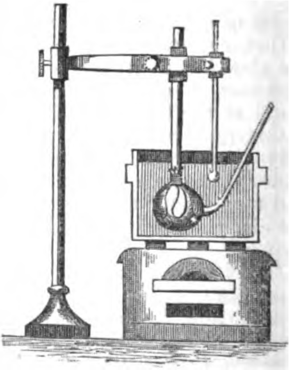

Fig. 12.

after which the neck is broken off beneath the surface of water, which has been boiled and cooled out of contact with the air, or (better) mercury. The liquid enters the globe, and, if the expulsion of the air by the vapour has been complete, fills it; if otherwise, an air-bubble is left, whose volume can be easily ascertained by pouring the liquid from the globe into a jar graduated in cubic inches, and then refilling the globe, and repeating the same observation; the capacity of the vessel is thus at the same time known, and these are all the data required. An example will render the whole intelligible.

Determination of the density of the vapour of Acetone.

Capacity of globe	31·61 cubic inches.
Weight of globe filled with dry air at 52° F., and 30·24 inches barometer	2070·88 grains.
Weight of globe filled with vapour at 212° F., temperature of bath at the moment of sealing the point, and 30·24 inches barometer	2076·81 grains.
Residual air at 45° F., and 30·24 inches barometer	0·60 cubic inches.

31·61 cubic inches of air at 52° F., and 30·24 inches barometer	32·36 cubic inches.
At 60° F., and 30 inches barometer, weighing	10·035 grains.
Hence, weight of empty globe, 2070·88 — 10·035	2060·845 grains.

0·6 cubic inch of air at 45° F. = 0·8 cubic inch at 212° F.; weight of which by calculation = 0·191 grain.

31·61 — 0·8 = 30·81 cubic inches of vapour at 212° F. and 30·24 inches barometer, which, *on the supposition that it could bear cooling to* 60° F. *without liquefaction*, would, at that temperature, and under a pressure of 30 inches barometer, become reduced to 24·18 cubic inches.

Hence,

Weight of globe and vapour	2076·810	grains.
„ residual air	0·191	„
	2076·619	„
Weight of globe	2060·845	„
Weight of the 24·18 cubic inches of vapour	15·774	„
Consequently, 100 cubic inches of such vapour must weigh	65·23	„
100 cubic inches of air, under similar circumstances, weigh	31·01	„

$\frac{65{\cdot}23}{31{\cdot}01} = 2{\cdot}103$, the sp. gr. of the vapour in question, air being taken as unity.

129. "In the foregoing statement a correction has been, for the sake of simplicity, omitted, which, in very exact experiments, must not be lost sight of, viz., the expansion and change of capacity of the glass globe by the elevated temperature of the bath. The density so obtained will be always on this account a little too high. The error to which the mercurial thermometer is, at high temperatures, liable, tends in the opposite direction."*

130. The following very simple and (for most chemical purposes) sufficiently accurate formula, will give the density of a vapour, from an experiment conducted as above, in a minute or two; and will, even when it is intended subsequently to recalculate the experiment with all the corrections, be found useful to determine whether an experiment has been successful.

D = the required density of the vapour;

P = difference in weight between globe and air, and globe and vapour;

V = capacity of balloon in cubic centimetres;

v = residual air;

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* "Manual of Chemistry," by Fownes.

n_t = weight of one cubic centimetre of air, at temperature at which the globe filled with air was weighed;

n_t^1 = weight of one cubic centimetre of air, at temperature of sealing the globe.

We have, therefore,—

$$D = \frac{P + V n_t}{(V - v) n_t^1} \, ^{*}$$

131. *Application of a knowledge of the specific gravity of the vapour to control the analysis of a substance.*—If we know the density of a compound substance we can ascertain whether the *empirical formula*,† that is, the *relative proportions of the equivalents* of the constituents, which have been deduced from the quantitative estimation of the elements of the substance, be correct; for, if the analysis of a substance and the formula deduced from it be correct, the vapour density *found by experiment* must correspond with *that calculated* from the formula. *If we know the specific gravity of a compound* (which may be regarded as the weight of one volume of the gaseous compound), *and its composition by weight, we can calculate the composition by volume*, and therefore, of course, its specific gravity. Example.—We have seen that the density of acetone-vapour, by experiment, is 2·103, and the analysis of the compound shows that its composition by weight is 62·07 of carbon, 10·34 of hydrogen, and 27·59 of oxygen, in 100 parts. In order to calculate the composition by volume and specific gravity, we must calculate the quantity of carbon, hydrogen, and oxygen in 2·103 of acetone.

If 100 parts	contain	62·07	carbon,	2·103	contain	1·30533.
,,	,,	10·34	,,	,,	,,	0·21745.
,,	,,	27·59	,,	,,	,,	0·58021.

The specific gravity, or weight of volume of carbon-vapour, is assumed to be 0·42139; 1 vol. of hydrogen weighs ·0693, and 1 vol. of oxygen weighs 1·1093; it is, therefore, evident that 1 vol. of the vapour of acetone contains,—

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[*] Liebig's "Handbook of Organic Analysis."

[†] See the author's "First Step in Chemistry," p. 239, 3rd Edition.

3 vols. (hypothetical) vapour of carbon -	1·26417
3 vols. of hydrogen - - -	0·20790
½ vol. of oxygen - - - -	0·55460
Theoretical sp. gr. of the vapour of acetone	2·02667

132. The composition by volume of a substance, and its density, can also be calculated from the formula in the following way:—Example: The formula of acetone, deduced from the analysis, is $C_3 H_3 O$; if we assume that the equivalent weight of hydrogen is represented by 1 vol., and that the equivalent weight of carbon is represented by 1 vol., then the equivalent weight of oxygen is represented by half a volume. Upon these assumptions the following calculation is made for the purpose of ascertaining how far the formula of acetone agrees with the vapour density:—

3 eqs. of carbon-vapour represent 3 vols., which weigh - -	$0·42139 \times 3 = 1·26417$
3 eqs. of hydrogen gas represent 3 vols., which weigh - -	$0·06930 \times 3 = 0·20790$
1 eq. of oxygen gas represents ½ vol., which weighs - -	$1·10930 \div 2 = 0·55460$
Theoretical sp. gr. of the vapour of acetone *	2·02667

133. By the aid of the vapour density obtained by experiment, we are enabled to ascertain whether we have deduced from the analysis of a substance a correct empirical formula, that is, whether the formula gives the correct atomic proportion of the elements; but the density does not enable us to decide what is the atomic weight of the compound. For instance, by the aid of the vapour density of acetone we find that the carbon, hydrogen, and oxygen in that compound are in the atomic ratio of 3 atoms of carbon, 3 of hydrogen, to 1 of oxygen; but whether the rational formula of acetone is $C_3 H_3 O$, or $C_6 H_6 O_2$, or $C_9 H_9 O_3$, the vapour density does not enable us to decide.

134. If the experimental density, and that obtained by

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* The difference between the theoretical number and the number found by experiment is due, in part, to slight errors which always occur in determinations of this kind, but there are other causes, which it is not necessary here to notice, which assist in producing the difference.

calculation, are the same, it shows that the constituents of the compound are condensed into one volume. But if the calculated density is double that of the density obtained by experiment, it shows that the constituents are condensed into two volumes, &c.

135. All assumptions may be dispensed with in calculating the density, if we first obtain the atomic measure by dividing the atomic weight by the specific gravity (111); the quotient will coincide or approximate very closely with one of the following numbers (if the formula and vapour density be correct), 2·41, 7·23, 14·66, or 28·92, according as the established formula represents a condensation to ⅓, 1, 2, or 4 volumes, taking the atom of oxygen to occupy one volume. If we then divide the atomic weight by the number representing the atomic measure, we obtain the theoretical density (111), which ought to correspond with that obtained by experiment.

EXERCISES.

65. What would be the weight of 1 cubic cent. of air at 10° C. and at the standard pressure?

66. What would be the weight of 20 cubic cent. of air at 15° C. and at the standard pressure?

67. What would be the weight of 15 cubic cent. of air at 20° C. and at 740 m.m.?

68. What would be the weight of 100 cubic cent. of air at 0° C. and 750 m.m.?

69. The following observations were made in determining the sp. gr. of a vapour by Gay Lussac's method: calculate the sp. gr. of the vapour from these data:—

Weight of liquid used - -	0·0366 grams.
Observed volume of vapour - -	18·7 cubic cent.
Height of barometer - - -	760·3 m. m.
Height of mercury in graduated vessel	109·2 ,,
Temperature - - -	100° C.

70. In the determination of the sp. gr. of the vapour of acetic ether by Dumas' method, the capacity of the globe was 305 cubic centimetres; its weight, when filled with air at 10° C., was 36 grammes; the weight of the globe filled with vapour at 100° C., which was the temperature at the moment of sealing, was 36·488 grams.; the

volume of residual air was 10 cubic cent. What was the experimental sp. gr. of the vapour?

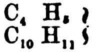
71. In the determination of the sp. gr. of the vapour of bromide of propylene ($C_6 H_6 Br_2$) by Dumas' method, the capacity of the globe was 204·5 cubic cent.; its weight, when filled with dry air at 22·25° C., was 33·2504 grams.; the weight of the globe filled with vapour at 198° C., which was the temperature at the moment of sealing, was 34·0879 grams.: the volume of the residual air was 4 cubic cent. What was the experimental sp. gr. of the vapour? and calculate the theoretical density from the formula.

72. The following observations were made in determining the sp. gr. of the vapour of amyl by Gay Lussac's method: calculate the sp. gr. of the vapour from these data:—

Weight of liquid used - -	0·1670 grams.
Observed volume of vapour - -	46·5 cubic cent.
Temperature - - -	190·5° C.
Height of barometer - -	738·1 m.m.
Height of mercury in graduated glass	10·0 „

73. The following observations were made in determining the sp. gr. of a vapour by Gay Lussac's method: calculate the sp. gr. of the vapour from these data:—

Weight of liquid employed - -	0·0863 grams.
Observed volume of vapour - -	39·8 cubic cent.
Temperature - - - - - -	100° C.
Height of barometer - - - -	733·8 m.m.
Height of mercury in graduated glass	31·0 „

74. In the determination of the sp. gr. of the vapour of amylate of ethyl,  $\left.\begin{matrix}C_4 & H_5\\ C_{10} & H_{11}\end{matrix}\right\} O_2$, by Dumas' method, the capacity of the globe was 377 cubic cent.; its weight, when filled with dry air at 10° C., was 93·779 grams.; the weight of the globe filled with vapour at 135·5° C., which was the temperature at the moment of sealing, was 94·6755 grams.; the volume of residual air was 3 cubic cent. What was the sp. gr. of the vapour by experiment? and calculate the theoretical density from the formula.

75. What is the composition, by volume and theoretical sp. gr., of butylic alcohol, its percentage composition by weight being 64·86 of carbon, 13·51 of

hydrogen, and 21·63 of oxygen; and its vapour density, by experiment, being 2·589?

76. What is the composition, by volume and theoretical sp. gr., of iodide of butyl, its percentage composition by weight being 26·22 of carbon, 4·91 of hydrogen, and 68·87 of iodine; and its vapour density, by experiment, being 6·217?

77. In the determination of the sp. gr. of the vapour of ethylate of methyl, $\left.\begin{matrix}C_4 H_5\\C_2 H_3\end{matrix}\right\}O_2$, the following observations were made:—

Weight of globe and air at 12° C. and 30·05 inches bar. - - - = 53·624 grams.
Weight of globe and vapour (the temp. = 23·5° C., and bar. = 30·05 inches at the moment of sealing) - = 54·179 „
Capacity of globe - - - - = 438 cubic cent.
Residual air at 16° C., and 30·05 bar. = 23 „

Calculate the density by experiment, according to the plan after which the vapour of acetone is calculated (page 65).

136. The sp. gr. of a gas can be calculated from its atomic weight, or its atomic weight from its sp. gr., as they are necessarily related to each other. The sp. gr. of a body in a state of vapour is obtained by multiplying the atomic weight of the body by 1105·6, the sp. gr. of oxygen, and dividing by 8, *if we take oxygen as the standard.* The number thus found must then be divided by the number of volumes which are known to compose the combining measure. *If we take hydrogen as the standard,* we must multiply the atomic weight of the body we desire to find the sp. gr. of by 1, and divide by 1; the quotient will be the sp. gr. of the body, if it be a monatomic gas; if it be a diatomic gas, the quotient must be multiplied by 2; in other words, the quotient must be multiplied by the number of volumes which are known to compose the combining measure of the vapour.

MISCELLANEOUS EXERCISES.

78. In what proportions by volume do ammonia ($N H_3$) and hydrochloric acid combine to form chloride of ammonium, the combining measure of oxygen being

taken as one volume? and what is the atomic measure of chloride of ammonium? The sp. gr. of ammonia is 0·596, the sp. gr. of hydrochloric acid is 1·247, and the sp. gr. of chloride of ammonium is 0·89 (air = 1).

79. One volume of a gas composed of carbon and hydrogen consumed 6½ times its volume of oxygen, and generated 4 times its volume of carbonic acid: how many volumes of hydrogen, and how many volumes of carbon-vapour, were condensed into one volume of the gas, and what was the theoretical density of the gas?

80. The atomic weight of hydrogen being 1, and its sp. gr. being 1, what will be the sp. gr. of phosphorus, its equivalent being 31?

81. The atomic and specific weight of hydrogen being 1, what will be the sp. gr. of chlorine, its equivalent being 35·5?

82. The atomic weight of oxygen being 8, and its sp. gr. being 1105·6, what will be the sp. gr. of nitrogen, its equivalent being 14?

83. The atomic weight of oxygen being 8, and its sp. gr. being 1105·6, what will be the sp. gr. of sulphur, its equivalent being 16?

84. The sp. gr. of hydrochloric acid being 1·247, that of hydrogen being 0·0692, and that of chlorine being 2·47, what is the percentage composition by weight of the acid?

85. The sp. gr. of olefiant gas being 0·981, that of hydrogen being 0·0692, and that of carbon vapour being 0·418, what is the percentage composition by weight of olefiant gas?

86. One hundred measures of a gaseous compound of carbon and hydrogen were mixed with 200 measures of oxygen in the eudiometer, and the mixture was exploded by the electric spark: 100 measures of a gas remained after the explosion, which was entirely absorbable by a solution of potash: what was the composition of the gas by volume; what was its percentage composition by weight; and what was its formula? The density of the gas was 0·559.

87. One hundred measures of a gaseous compound of carbon and hydrogen were mixed with 300 measures of oxygen in the eudiometer, and the mixture was exploded by the electric spark: 200 measures of a gas remained after the explosion, which was entirely absorbable by a

solution of potash: what was the composition of the gas by volume; what was its percentage composition by weight; and what was its formula? The density of the gas was 0·981.

88. In what proportions by volume do cyanogen and ethyl ($C_4 H_5$) combine to form cyanide of ethyl, the combining measure of oxygen being taken as one volume? and what is the atomic measure of cyanide of ethyl? The sp. gr. of cyanogen is 1·806; that of ethyl is 2·004; and that of cyanide of ethyl is 0·788 (air = 1).

89. One volume of a gas composed of carbon and hydrogen consumed 3½ times its volume of oxygen, and generated 2 volumes of carbonic acid: how many volumes of carbon-vapour, and how many volumes of hydrogen, were condensed into one volume of the gas, and what was the theoretical density of the gas?

90. What is the composition, by volume and theoretical density, of amylene ($C_{10} H_{10}$); and how many volumes of oxygen would one volume of it require for its combustion; and how many volumes of carbonic acid would be generated?

91. How many volumes of oxygen would one volume of olefiant gas require for its combustion; and how many volumes of carbonic acid would be generated?

92. A gas made from coal had the following percentage composition:—

Hydro-carbons absorbable by fuming sulphuric acid	10·81*
Light carburetted hydrogen	41·99
Hydrogen	35·94
Carbonic oxide	10·07
Carbonic acid	1·19
Nitrogen Oxygen	traces.
	100·00

One volume of the hydro-carbons absorbable by sulphuric acid, when exploded with oxygen, generated 2·8 volumes of carbonic acid:† was olefiant gas the only hydro-carbon present? If other hydro-carbons were present, state what the 10·81 is equal to in olefiant gas.

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* Olefiant gas, and almost all the hydro-carbons having the general formula $C_n H_n$, are completely absorbed by fuming sulphuric acid.

† The illuminating power of coal-gas is exclusively due to the hydro-carbons of the form $C_n H_n$; and as these vary in their light-giving powers,

93. What bulk of air would be required for the combustion of 100 grains of a coal of the following composition; what products would result from the combustion, and what would be the weight of each product, and what the bulk of the carbonic acid produced?

Carbon	71·08
Hydrogen	4·88
Nitrogen	0·95
Sulphur	1·37
Oxygen	17·87
Ash	3·85
	100·00

94. What bulk of air would be required for 100 grains of a peat of the following composition; what products would result from the combustion, and what would be the weight of each product, and what the bulk of the carbonic acid produced?

Carbon	58·69
Hydrogen	4·97
Nitrogen	1·47
Oxygen	32·88
Ash	1·99
	100·00

95. Coal gas made from Lismahago Cannel had the following percentage composition:—

Hydron-carbons absorbable by fuming sulphuric acid	16·31
Light carburetted hydrogen	42·01
Hydrogen	26·84
Carbonic oxide	14·18
Carbonic acid	0·66
Oxygen Nitrogen	traces.
	100·00

---

in direct proportion to their richness in carbon, it follows that their illuminating value can only be estimated by determining the amount of carbon which a given volume of them contains.

One volume of the hydro-carbons absorbable by sulphuric acid, when exploded with oxygen, produced 3·47 volumes of carbonic acid; was olefiant gas the only hydro-carbon present? If olefiant gas was not the only hydro-carbon present, state what the 16·31 is equal to in olefiant gas.

96. What bulk of air would be required for 100 grains of a coal of the following composition; what products would be produced by the combustion; what would be the weight of each product; and what the bulk of the carbonic acid produced?

Carbon - - - -	89·78
Hydrogen - - -	5·15
Nitrogen - - -	2·16
Sulphur - - -	1·02
Oxygen - - -	0·39
Ash - - - -	1·50
	100·00

97. In the determination of the sp. gr. of the vapour of eugenic acid ($C_{20} H_{12} O_4$) the capacity of the globe was 275·5 cubic cent.; excess of weight of globe, 0·7030 gram.; temperature of vapour, 274° C.; temperature of air, 18° C.; residual air, 1·0 cubic cent. What was the experimental sp. gr. of the vapour?

98. What is the atomic measure and theoretical density of the vapour of eugenic acid?

137. *Buoyancy of the air.*—The general fact, that air, like liquids, buoys up all bodies immersed in it, may be illustrated by means of the apparatus represented in Fig. 13. It consists of a closed

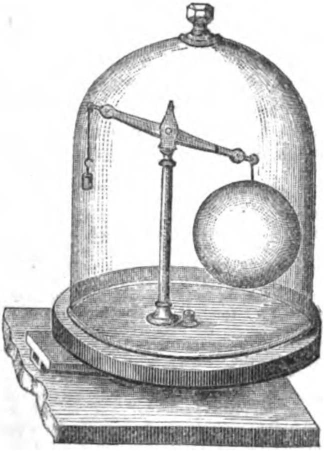

Fig. 13.

globe, suspended to one arm of a delicate balance, equipoised by a weight suspended to the other. The two are in equilibrium in the air, but only because the globe, being larger than the weight, is buoyed up by a greater force. If, now, the apparatus is placed upon the plate of an air-pump and covered with a glass bell, we shall find, on removing the air, that the globe will preponderate, as is shown in the figure. By removing the air we increase the apparent weight both of the globe and of the counterpoise by just the weight of the air displaced by each; but as the globe is much the largest, we increase its weight more than that of the smaller brass counterpoise, and hence the result. If we allow the air to re-enter the bell, it will buoy up the globe, as before, so much more than the counterpoise, as to restore the equilibrium.

138. *Weight of a body in air.*—An important consequence of the principle just illustrated is evident. The balance does not give us the true relative weight, W, of a body, but a slightly different weight, depending on the weight of air displaced by the body, compared with the weight of air displaced by the brass or platinum weights used in weighing. As the volume of these weights is generally less than that of the body, the weight indicated by the balance is almost always too small; but when the volume of the weights is greater than that of the body, the weight indicated by the balance is too large. When the two volumes are equal, the balance will indicate the same weight in air as in a vacuum. It is easy to ascertain the correction which it is necessary to add or to subtract from the weight of a body in air in order to obtain its true weight.[*]

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[*] "The weight of the displaced portion of air may be easily ascertained if the specific gravity of the body be known; for, from the observed weight of the body, we can calculate directly the weight of an equal bulk of water, and $\frac{1}{817}$th of this weight will give the weight of a corresponding bulk of air at mean temperature and pressure. This weight must be added to that actually found; at the same time, a similar and opposite correction will be required for the metallic weights used in the experiment, because they will also appear to be lighter than they really are; and an amount of weight greater than the true one will be required to effect the counterpoise. If, therefore, the weights have the same specific gravity as the body counterpoised, the two corrections will neutralize each other; but if, as in weighing gases, there is a great difference between them, the correction will be one of importance. The true weight sought will be thus obtained:—*Add to the weight of the body in air, the weight of the bulk of air which it has displaced, and deduct from this the weight of the bulk of air displaced by the weights employed.*"—*Miller.*

139. It must be remembered that the brass and platinum weights which are used in delicate determinations of weight are only standard when in a vacuum. Let us, then, represent the various values as follows:—

W^1 = Weight of the body in air as estimated by standard weights; and also the weight of the standard weights themselves in a vacuum.
V^1 = Volume of the standard weights in cubic centimetres.
V = Volume of the body in cubic centimetres.
w = Weight of one cubic centimetre of air at the time of the weighing.
W = Weight of the body in a vacuum,—which we wish to find.

We can now easily deduce the following values:—

V^1w = Buoyancy of air on the weights.
Vw = Buoyancy of air on the body.
$W^1 - V^1w$ = Actual weight of standard weights in air.
$W - Vw$ = Actual weight of body in air.

Since these weights just balanced each other, we have—

$$W - Vw = W^1 - V^1w; \text{ or } W = W^1 + w\,(V - V^1).$$

140. The correction $w\,(V - V^1)$ which must be made to the weight determined by a balance in air in order to obtain the weight in a vacuum, is evidently additive when the volume of the body is greater than that of the weights, and subtractive when these conditions are reversed. When the volumes are equal, the correction becomes 0.

141. In all ordinary cases of weighing, the correction is so small that it may be neglected without sensible error; but it becomes of the greatest importance in determining the weight of a gas. In such cases, we have to determine the weight of a large glass globe, when completely vacuous, and when filled with gas; and it not unfrequently happens, that the buoyancy of the air is greater than the weight of the gas itself, and it is always a considerable part of it. If the buoyancy of the air is the same when the globe is weighed in its vacuous condition and when filled with gas, it would not affect the weight of the gas, which would be obtained by subtracting the first weight from the last. But, unfortunately, the buoyancy is constantly changing;

and it is, therefore, necessary to determine the amount carefully at each weighing, and reduce the weights of the globe in the two conditions to what they would be if the experiments had been made in a vacuum.

142. When the temperature is 0° C., and the barometer stands at 76 c. m., and when the air contains neither vapour of water nor carbonic acid, *w* is equal to 0·001293 grams. Were the atmosphere always in this condition, nothing would be easier than to calculate the actual weight of a body from the weight found by weighing in this normal atmosphere. But this is far from being the case; for the temperature, the pressure, and the composition of the atmosphere, are changing at each moment, and the value of *w* varies with all these atmospheric changes.

143. It is frequently possible to conduct the process of weighing in such a way that the correction for the buoyancy of the atmosphere, always somewhat uncertain, may be avoided. For example, in weighing a gas, instead of equipoising the glass globe when empty, by means of ordinary weights, we may equipoise it by means of a second globe, hermetically closed, and having the same volume as the first, in the manner represented in Fig. 14. It is evident that in this case, whatever may be the buoyancy of the atmosphere, it will equally affect both globes, and we shall only have to consider the buoyancy of the air on the small weights necessary to restore the equilibrium after the globe is filled with the gas to be weighed; but this is so small that it may always be neglected.*

144. DENSITIES OF GASES.—*Regnault's method.*—The most accurate method of determining the specific gravity of a gas is due to Regnault; it consists in determining with the apparatus, Fig. 14, the weight of the given gas which a large balloon will contain at 0° C. and 76 c. m., and then dividing this weight by that of an equal volume of air previously determined in the same way. The balloon in which the gas is weighed is counterpoised, not entirely by weights, but chiefly, as we have already stated, by another balloon of the same kind of glass, and of the same bulk. To do this, it is necessary to determine the volume of air displaced by the balloon in which

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* Cooke's "Chemical Physics."

the gas is to be weighed, and which we will call A. It is to be filled with water, and then weighed in water of the same temperature. The apparent weight of the balloon in water is so small, that this may be effected on the balance to be used for the densities. The balloon is now to be removed, and weighed, after wiping, but still filled with water, on a strong balance capable of indicating one decigramme. The difference in the two weighings is equal to the weight of water displaced by the external volume of the balloon. Another balloon, B, Fig. 14, of nearly the same capacity as A, but, preferably, a little smaller than that of the first and its stopcock, and made of the same kind of glass, is taken, and has connected to it a brass mounting, terminating in a hook, to enable it to be suspended from the balance-pan. If the united weight of the water displaced by the balloon, B, and its mounting, is less by *n* grammes than the weight of the water displaced by the balloon, A, we must attach to B a glass tube closed

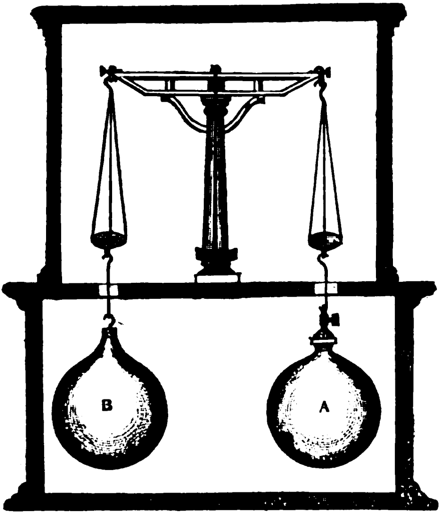

Fig. 14.

at each end, and having an exterior bulk = n cent. cub. of water.*

145. The engraving, Fig. 14, shows the method of suspending the balloons beneath the scale-pans of the balance, in a chamber closed with glass doors to prevent currents of air. The balance, although large, is of great delicacy; for when charged with one kilogramme in each pan, it permits with certainty an appreciation of half a millegramme. The balloons employed have a capacity of about 10 litres.

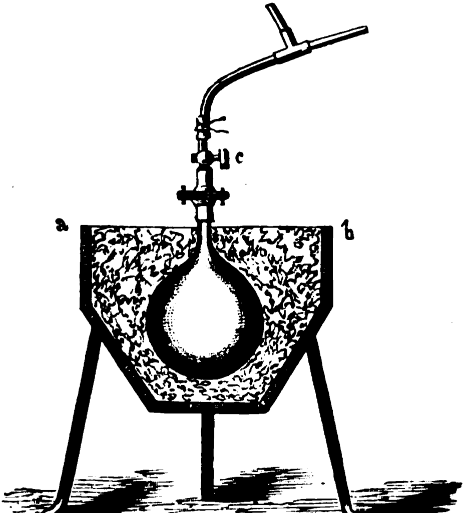

Fig. 15.

146. The balloon, A, has a stopcock attached to it, which allows it to be connected either with a three-way tube communicating with the gas-holder, or with the air-pump. The air having been removed as completely as possible, the gas is allowed to enter; but as a small amount of air still

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* Because 1 cent. cub. of water weighs 1 gramme.

remains, the operation is to be repeated twice. Previous to the third time of filling the globe, it is, after as complete exhaustion as possible, to be placed in a case, *a b*, Fig. 15, and covered with melting ice; the cock being opened, the globe is allowed to fill with gas, and when full, a momentary communication is made with the atmosphere to equalize the pressure; the cock, *c*, is closed, the globe removed, wiped with a damp cloth to prevent electrical excitation, which might cause serious errors in the weighing, and suspended on the balance. It is not weighed until two hours have elapsed, so as to permit the temperature to become the same as that of the balance case, and thus obviate currents of air, and also that its surface may be covered with the normal amount of humidity. After careful weighing, the balloon is placed anew in the case, *a b*, Fig. 15, surrounded with ice, and the gas removed by the pump.

It is necessary now to ascertain both the atmospheric pressure and the elastic force of the gas remaining in the balloon. For this purpose, an instrument called a barometric manometer, is made use of. It consists of two tubes, A B and C D, Fig. 16, attached to a support, which is secured perpendicularly to a wall. The tube, A B, is a barometer of 20 m.m. interior diameter; the metal in the tube having been carefully boiled, it is inverted in a cistern of dry mercury. This cistern is a box divided into two parts, the smaller of which serves for the cistern of the barometer. Into the second compartment is plunged the tube, C D, which has the same diameter as A B. C D is capable, by means of a leaden tube, *a b*, of being placed in communication with the balloon.

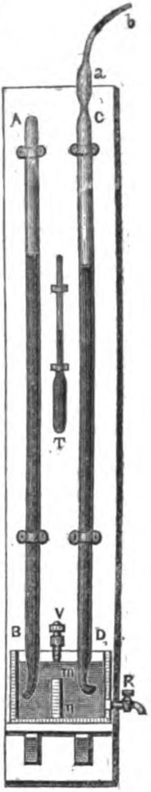

Fig. 16.

147. When it is intended to ascertain the atmospheric pressure by means of this instrument, mercury is poured into the cistern until it rises above the level of the division, *m n*. The double-pointed screw, V, is then adjusted, until its lower end just touches the surface of the mercury. If, now, we measure, by means of a cathetometer, the difference of level between the surface of the mercury in the barometer, and the upper point of the screw, and add to this the length of the screw previously ascertained, we have the height of a column of mercury exactly balancing the atmospheric pressure. The tube, C D, of the manometric apparatus, is, as we have said, to be placed in communication with the air-pump and the balloon, by means of the three-way tube and the leaden pipe, *a b*. The gas having been removed, the cock communicating with the air-pump is closed, and the difference of level between the two columns of mercury in the tubes, A B and C D, is measured by a cathetometer. This difference is the measure of the elastic force of the gas remaining in the balloon. A thermometer, T, indicates the temperature at the time of the experiment.

148. The division, *m n*, in the cistern is necessary, in order to prevent air reaching the barometer, in consequence of the great oscillations in the level of the mercury during experiments. The balloon, thus again exhausted, and having the elasticity of its residual gas known, is to be closed, removed, wiped, and weighed as before.

149. The difference, $P - p$, between the two weighings, represents the weight of the gas, which at 0° C. = 32° F. fills the balloon under a pressure equal to the barometric pressure, H, observed at the moment of closing the cock, diminished by the elastic force, h, of the gas remaining in the balloon after making the exhaustion. The weight of the gas at 0° C., and under the normal pressure of 760 m.m. (29·922 inches), is obtained by the formula*—

$$(P - p)\,\frac{760}{H - h}.$$

150. *Bunsen's method.*—The specific gravities of various gases are represented by the weights which equal volumes of these gases possess. As the volume occupied by a

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* From Greville Williams's excellent "Handbook of Chemical Manipulation."

given weight of any gas is dependent upon the variations of the force of gravity accompanying change of geographical latitude, or elevation above the sea's level, all gases, of which the absolute volumes are required, must be reduced to the same latitude and elevation above the sea, and to the same barometric pressure and temperature.

151. According to the most accurate experiments, for which we are indebted to the classical labours of Regnault, one gramme of atmospheric air at the level of the sea, in the 45th degree of latitude, at 0° C., and under a pressure of $0{\cdot}76^{m.}$ of mercury, occupies a volume of 773·526 cubic centimetres. In the latitude 52° 36′—as, for instance, in Berlin,—a gramme of dry air at 0° C., and under a pressure of $0{\cdot}76^{m.}$, occupies exactly 773 cubic centimetres.

152. The accuracy of gasometric determinations is seldom so great, that the differences resulting from the variation of gravitation extend beyond the limits of the possible observational errors. Hence, excepting in *normal* determinations, when the greatest accuracy is required, the volume of one gram. of dry at 0° C., and $0{\cdot}76^{m.}$ pressure of mercury, may be represented in our latitudes by 773 cubic centimetres; and the specific gravity of a gas may be defined to be, the weight in grammes of gas which, under the same conditions, occupies a space of 773 cubic centimetres.

153. In cases in which a normal determination is not required, a common light flask, *g*, Fig. 17, is employed for measuring the volume of gas of which the specific gravity is to be estimated.

The volume of the flask should be about 200 or 300 cubic centimetres, and the neck, *a*, thickened before the glass blow-pipe, must be drawn out so as to have an aperture of the thickness of a straw, into which a glass stopper is ground air-tight by means of emery and turpentine. Through this neck, which is furnished with an etched scale in millimetres, mercury is poured, by means of a funnel reaching to the bottom of the flask, until the whole is filled. As soon as this is accomplished, the flask is transferred, with its mouth downwards, into the mercury trough, A A, and gas is allowed to enter, until the level of mercury in the neck of the flask stands a few millimetres higher than that in the trough. In order to

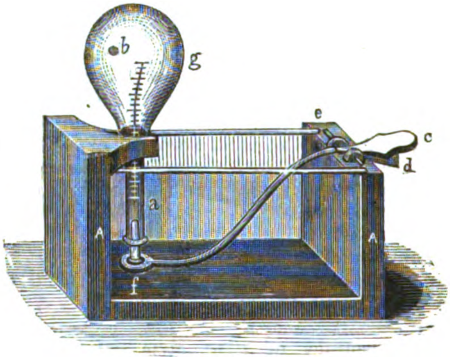

Fig. 17.

secure the absence of all gaseous impurities, this gas is evolved from as small a vessel as possible, and allowed to enter the flask through a narrow delivery tube, and in the moist state. The gas is dried in the flask itself by a small piece of fused chloride of calcium, *b*, which had previously been made to crystallize on the side of the flask by bringing it in contact with a single drop of water, and alternately heating and cooling the glass. This small piece of chloride of calcium serves also to free the mercury and the sides of the flask from its adhering moisture. In order to be able to close the flask at any time without warming it with the hand, the little lever, *c f*, is employed. On the lower end, *f*, of this lever the stopper is so fastened in a cork, that it passes into the neck of the flask without closing it, and the lever is held in its right place by a wedge, *d*, pushed under the finger-plate, *c*. As soon as the apparatus has attained the constant temperature, *t*, at the barometric pressure, P, the volume, V, of the gas, and the height, *p*, of the column of mercury rising above the level of the metal in the trough, are observed with the cathetometer telescope. If the observed volume of gas in cubic centimetres, reduced from a table of capacity, be represented by V_1, this volume, at 0° C., and 0·76 pressure, becomes in cubic centimetres,—

$$V_2 = \frac{V_1 (P - p)}{0{\cdot}76\ (1 + 0{\cdot}00366\ t)}.$$

154. It is now only necessary to determine the weight, G_2, of this volume, V_2. This is obtained in the following manner:—The wedge, *d*, is taken away; the flask is thereby closed, and by withdrawing the pin, *e*, it can then be removed, together with the lever, *c f*, from the trough. After having been most carefully freed from all adhering matters, and having attained the temperature, t_1, of the balance, by the pressure, P_1, the flask can be weighed. Let *G* represent the weight in grammes thus found. The glass stopper is now removed, and replaced by a caoutchouc tube, connected with a drying tube, *b*, Fig. 18. The apparatus thus arranged is placed under the receiver of an air-pump, and the air so often withdrawn and admitted until all the gas has been replaced by dry air. If this weight amounts to G_1 grammes, the weight, G_2, of the volume of gas, V_2, measured in the flask, is equal to—

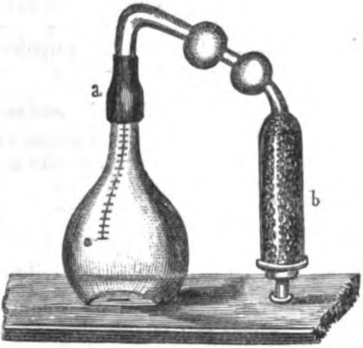

Fig. 18.

$$G_2 = G - G_1 + \frac{V_1\ P_1}{773 \times 0{\cdot}76 \times (1 + 0{\cdot}00366\ t_1)}*$$

155. From this value, G_2, the specific gravity is obtained by the help of the following formula:†—

$$S = 773\ \frac{G_2}{V_2}$$

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* The unequal specific gravity of the glass and mercury on the one hand, and the metal weights on the other, is not considered in this calculation, as the inaccuracy thus introduced is inconsiderable, in comparison to the observational errors.

† From Bunsen's "Gasometry," translated by Roscoe.

EXERCISES.

99. Calculate the weight of one litre of dry air at 0° C. and 76 c. m. from the following determination by Regnault:—

Globe full of air, and surrounded by ice.

Height of barometer at the time of closing the stop-cock - - - - - -	76·119 c. m.
Weight added to globe to equipoise it in balance - - - - - - -	1·487 gram.

Globe exhausted of air, and surrounded by ice.

Tension of air remaining in globe, as indicated by the manometer at the moment of closing the stop-cock - - -	0·843 c. m.
Weight required for equipoise - -	14·141 gram.

100. Calculate the weight of one litre of hydrogen at 0° C. and 76 c. m. from the following determinations of Regnault:—

Globe full of gas, and surrounded by ice.

Height of barometer at the time of closing the stop-cock - - - - - -	75·616 c. m.
Weight added to globe to equipoise it in balance - - - - - - -	13·301 gram.

Globe exhausted of gas, and surrounded by ice.

Tension of gas remaining in globe, as indicated by the manometer at the moment of closing the stop-cock - - -	0·340 c. m.
Weight required for equipoise - -	14·1785 gr.

101. Calculate the weight of one litre of carbonic acid at 0° C. and 76 c. m. from the following determinations by Regnault:—

Globe full of gas, and surrounded by ice.

Height of barometer at the time of closing the stop-cock - - - - - -	76·304
Weight added to globe to equipoise it in balance - - - - - - -	0·6335 gr.

Globe exhausted of gas, and surrounded by ice.

Tension of gas remaining in globe, as indicated by the manometer at the moment of closing the stop-cock	0·157 c. m.
Weight required for equipoise	20·211 gram.

102. The following observations were made in determining the vapour density of gaseous bromide of methyl by Bunsen's method. From these data calculate the specific gravity of the gas.

Volume of gas	42·19 c. c.
Temperature of room	16·8° C.
Height of barometer	0·7464$^{\text{m.}}$
Height of the column of mercury above that in the trough	0·0243$^{\text{m.}}$
Weight of flask and gas	7·9465 gram.
Weight of flask and air	7·8397 „
Temperature in balance case	6·2° C.
Height of barometer at the time of weighing	0·7421$^{\text{m.}}$

103. The following observations were made in determining the density of a gaseous mixture by Bunsen's method. Calculate the density from these data.

Volume of gas	211·23 c. c.
Temperature of room	6·2° C.
Height of barometer	0·7609$^{\text{m.}}$
Height of the column of mercury above that in trough	0·0194$^{\text{m.}}$
Weight of flask and gas	54·6213 gram.
Weight of flask and air	54·4838 „
Temperature in balance case	7·9° C.
Height of barometer at the time of weighing	0·7609$^{\text{m.}}$

104. The following observations were made in determining the density of a gas by Bunsen's method. Calculate from these data the density of the gas.

Volume of gas	210·2 c. c.
Temperature of room	19·7° C.
Height of barometer	0·748$^{\text{m.}}$
Height of the column of mercury above that in the trough	0·0172$^{\text{m.}}$

Weight of flask filled with gas - -	53·591	gram.
Weight of flask filled with air - -	53·5775	„
Temperature in balance case - -	20·5° C.	
Height of barometer at the time of weighing - - - - - -	0·748$^{m.}$	

156. GASEOUS ANALYSIS.—We shall conclude this chapter on volume combinations, by briefly describing the method by which the volume of each gas is determined in a gaseous mixture. The volumes of the separate constituents of a gaseous mixture can be ascertained, either by absorbing them by means of substances with which they combine or in which they dissolve, or by exploding those which are combustible with oxygen; by the absorptive plan the determinations are direct, by the other the gases are determined indirectly.

157. The following are some of the gases which admit of direct determination:—

Carbonic acid.
Oxygen.
Olefiant gas.
Carbonic oxide.

158. The following are the most important gases which are usually determined by the indirect method:—

Hydrogen.
Light carburetted hydrogen.
Carbonic oxide.

159. Nitrogen is neither absorbed nor does it undergo any alteration by the explosion, if the necessary precautions are taken; its quantity is therefore determined by measure after all the gases which admit of absorption have been removed, and also all the combustible gases, and the products which they yield by explosion.

160. The absorption materials were formerly used in the fluid state in gas analysis; the fluid form gave rise to such unconquerable errors, that Bunsen, by the substitution of substances in the dry state, has rendered this branch of analytical science the most exact; the solid substances are introduced in the form of little pistol bullets.

161. In all estimations of gases, it is necessary either always to operate with them perfectly dry or thoroughly saturated with moisture; in order to avoid all uncertainty and to save time, the original gaseous mixture is thoroughly saturated with water by introducing a

drop of water into the eudiometer before filling it with the gas, and in this saturated state the gas is first measured. It is necessary, in determining the volume of the gas, not only to observe the volume the gas occupies, but also the height of the mercury in the eudiometer above that in the trough; it is necessary also, in each determination of the volume, to observe the pressure and the temperature,—the barometer and thermometer must be placed in close proximity to the eudiometer; the observed volumes have to be corrected for temperature and pressure, and also for the tension of aqueous vapour, when the gas is measured moist, giving the corrected volumes at the normal temperature and pressure.

162. The room in which gas analyses are made ought to be exclusively devoted to that purpose; it ought to be cool, and not liable to any sudden changes of temperature. If the analyst does not use a telescope in reading off the volumes, he ought, when he approaches the eudiometer for this purpose, to do it as quickly as possible, as the heat evolved from the operator's body will speedily augment the volume of the gas. After removing any of the absorbing substances, or after an explosion, time must be allowed for the gas to return to the temperature of the room before the volume is determined.*

163. Carbonic acid is absorbed by means of a little bullet of caustic potash, which deprives the gas both of its carbonic acid and aqueous vapour. Olefiant gas † is absorbed by saturating a coke bullet with a mixture of anhydrous and monohydrated sulphuric acid; when the coke bullet is removed, it is necessary to introduce a bullet of potash to absorb the vapour of sulphurous acid and of anhydrous sulphuric acid, before the volume of the gas can be determined. Oxygen ‡ is absorbed either

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* Messrs. Frankland and Ward have invented a beautiful apparatus for gas analysis, in which the determinations are made entirely independent of the pressure and temperature of the external atmosphere, and the numerical expression of each volume actually read off is either the true and corrected volume, or a number from which such volume can be at once obtained by the most simple arithmetical process. For a description of this apparatus and mode of using it, the student is referred to the 6th volume of the "Quarterly Journal of the Chemical Society of London," or to Knights' "English Cyclopædia," divison "Arts and Sciences," vol. iv.

† Olefiant gas can be still more exactly determined by combustion with oxygen.

‡ Oxygen when present alone, or when mixed with nitrogen, is best determined by explosion with excess of hydrogen.

by a bullet of phosphorus, or a bullet of papier maché saturated with a concentrated solution of pyrogallate of potash. Whichever of the two absorptive materials is used, it is necessary after its removal to introduce a bullet of potash, before the volume of the gas can be determined. Carbonic oxide is most usually and more accurately determined by the indirect method; when it is desirable to determine it by the direct method, it is absorbed by introducing a bullet of papier maché saturated with a concentrated solution of subchloride of copper. After the removal of this bullet, a caustic potash one has to be introduced, to free the gas from the vapour of hydrochloric acid, before the volume of the gas can be determined. By the methods just described, the carbonic acid, oxygen, and olefiant gas were determined in the following exercises; in order to arrive at the quantities of each of the gases at the normal temperature and pressure, the student will simply have to correct the different volumes for temperature and pressure, and also, when the gas was moist, for the tension of aqueous vapour, giving the corrected volume at 0° C. and 1 metre pressure.

164. The determinations of the gases by the indirect method cannot well be conducted in the eudiometer in which the absorptions have been made, a portion, therefore, of the gaseous mixture, after the absorption of the absorbable gases, is transferred to another and somewhat longer eudiometer. After the volume of the gas in the long eudiometer has been carefully determined, it is mixed with at least twice its bulk of oxygen; after measuring the volume after the addition of oxygen, the gas is exploded by means of the electric spark. After the gas has cooled to the temperature of the room its volume is determined; the carbonic acid which has been formed by the explosion is then absorbed by a bullet of potash; and the volume, after the removal of the bullet, again determined. It is now necessary to ascertain how much oxygen gas still remains in the eudiometer after the explosion. For this purpose some pure hydrogen is conducted into the eudiometer, and after the volume of the hydrogen has been determined, the mixture is exploded by the electric spark. One-third of the volume of the gas which has disappeared is oxygen. The residual gas, still saturated with water, can now only contain nitrogen

and the excess of hydrogen, and by deducting the known amount of the latter, we determine the proportion of nitrogen present.

165. "To determine the amount of carbonic oxide, hydrogen, and light carburetted hydrogen, we employ in calculation the three quantities following, from the analysis:—

"1. The quantity of combustible gases which is obtained by subtracting the amount of nitrogen contained in the gaseous mixture in the large eudiometer.

"2. The quantity of oxygen consumed in the oxidation of the combustible gases. This we obtain by subtracting the excess of oxygen, as ascertained by explosion with hydrogen, from the amount originally added.

"3. The quantity of carbonic acid formed by the combustion.

166. "The calculation depends upon the fact that hydrogen consumes half its own volume of oxygen, and generates no carbonic acid; light carburetted hydrogen consumes twice its volume of oxygen, and generates its own volume of carbonic acid; whilst carbonic oxide consumes half its volume of oxygen, and generates its own volume of carbonic acid.

167. "If we represent—

The volume of the combustible gases present by A
The volume of oxygen consumed by - - B
The volume of carbonic acid generated by the explosion by - - - - - - - C

And if we represent the unknown quantities of hydrogen, light carburetted hydrogen, and carbonic oxide, by x, y, z, we obtain the following equations:—

$$x + y + z = A$$
$$\tfrac{1}{2}x + 2y + \tfrac{1}{2}z = B$$
$$y + z = C$$

"From these are deduced the following values for the unknown quantities, x, y, z:"—*

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* Dr. Playfair "On the Gases evolved during the Formation of Coal." The student will find in this paper a very clear account of the mode of proceeding to be adopted in the analysis of coal gas, and gases of a similar composition. The paper is printed in Vol. I. of the "Memoirs of the Geological Survey."

The most complete work on gas analysis is Bunsen's "Gasometry," translated by Roscoe.

We have already referred the student to Frankland and Ward's method.

$x = A - C$ $\quad y = \frac{2B - A}{3}$ $\quad z = C - \left(\frac{2B - A}{3}\right)$

168. If on the application of these formulæ to the results of an analysis, the value of any letter be either a small negative quantity or = 0, it follows that the gas denoted by the letter is not present in the mixture.

169. In the following exercises the student must correct the volumes for temperature, pressure, and also for tension of aqueous vapour when the gas is moist, giving the corrected volume at 0° C. and 1 metre pressure; he must give the proportion of the different gases in the quantity of the gaseous mixture used, and lastly the percentage composition of the gaseous mixture.

EXERCISES.

105. The following observations were made in analyzing a coal gas :—

——	Volume.	Temp. C.	Pressure.	Height of mercury above that in trough.
Gas used (moist) -	132·6	16·4°	756·3$^{\text{m.m.}}$	71·8$^{\text{m.m.}}$
After absorption of carbonic acid (dry) - - - -	127·7	16·4	756·1	77·2
After absorption of olefiant gas (dry)	121·3	16·3	756·0	83·6
After absorption of oxygen (dry) - -	118·1	16·3	756·0	89·9
Gas used (moist) -	149·6	16·0	756·1	423·6
After addition of oxygen (moist) -	280·1	16·2	756·2	311·7
After combustion (moist) - - -	205·7	16·1	756·2	367·1
After absorption of carbonic acid (dry) - - - -	163·6	16·1	756·4	409·4
After addition of hydrogen (dry) -	328·7	16·0	756·5	242·9
After combustion (moist) - - - -	136·3	16·0	756·5	436·7

106. The following observations were made in analyzing a gas collected from a coal mine:—

——	Volume.	Temp. C.	Pressure.	Height of mercury above that in trough.
Gas used (moist) -	112·1	15·5°	749·9$^{\text{m.m.}}$	67·9$^{\text{m.m.}}$
After absorption of carbonic acid (dry) - - - -	108·0	15·5	749·3	72·8
After absorption of oxygen (dry) -	...	...	...	...
Gas used (moist) -	130·4	16·1	748·9	276·9
After addition of oxygen (moist) -	317·8	16·1	748·9	91·5
After combustion (moist) - - -	194·9	16·0	748·7	212·5
After absorption of carbonic acid (dry) - - - -	110·6	13·5	746·7	296·5
After addition of hydrogen (dry) -	294·4	13·5	745·8	114·2
After combustion (moist) - - -	134·3	13·5	745·7	272·7

107. The following observations were made in analyzing a gas collected from a coal mine:—

——	Volume.	Temp. C.	Pressure.	Height of column of mercury above that in trough.
Gas used (moist) -	114·0	16·0°	761·4$^{\text{m.m.}}$	72·1$^{\text{m.m.}}$
After absorption of carbonic acid (dry) - - - -	111·4	15·8	760·6	74·7
After absorption of oxygen (dry) -	97·5	15·5	749·9	39·8
Gas used (moist) -	78·6	15·4	750·6	226·1
After addition of oxygen (moist) -	156·3	15·3	751·0	148·1

——	Volume.	Temp. C.	Pressure.	Height of column of mercury above that in trough.
After combustion (moist) - - -	130·0	15·5°	751·0$^{m.m.}$	174·7$^{m.m.}$
After absorption of carbonic acid (dry) - - - -	113·9	15·3	751·2	191·0
After addition of hydrogen (dry) -	273·2	14·6	752·3	32·2
After combustion (moist) - - -	163·8	14·4	752·3	140·7

108. Describe a method of analyzing a mixture of hydrogen, nitrogen, and carbonic acid.

109. Describe a method of analyzing a mixture of oxygen, nitrogen, and carbonic acid.

170. Before we close this chapter we must make a few additional remarks upon the use of vapour densities. Although a knowledge of the vapour density of a substance does not enable one to establish the rational formula of the body, yet if we can infer from analogy a certain ratio of condensation, we may make use of it in this way. All *known* hydro-carbons exhibit a condensation to four volumes.* All hydro-carbons which may hereafter be discovered will, therefore, have that formula assigned to them which gives for their atomic volume a condensation of four volumes, unless they should possess some marked characteristics which render it probable that they deviate from this rule. Example.—When Sir Robert Kane discovered mesitilol he was led, from its origin and other circumstances, to represent it by the formula $C_6 H_4$; but as this only corresponded to one volume, the formula $C_{18} H_{12}$ was afterwards assigned it, on account of its vapour density, boiling-point, and other circumstances. As nearly all known organic bodies exhibit a condensation to four volumes, it is usual to assign to bodies the formula which

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* Here the volume of the atom of the organic compound in the gaseous state is compared with the volume of one atom of oxygen.

gives for the atomic volume a condensation to four volumes, if this formula is justified by all the other circumstances. The original formula for acetone, as resulting from Dumas' and Liebig's analyses, was $C_3 H_3 O$, representing an equivalent of an acetate, minus an equivalent of a carbonate; a formula which, subsequently, when Dumas determined the density of the vapour of this liquid, was doubled, on the supposition that its equivalent corresponded to four volumes of vapour. The equivalent of any organic substance (corresponding to four volumes), multiplied by ·0346, or half the density of hydrogen, $H = 1$, gives its vapour density.*

171. As silicic acid gives a very small number of definite combinations it is very difficult to fix the equivalent of silicon. Some chemists assign to silicic acid the formula $Si O$, others regard it as $Si O_2$, and others again as $Si O_3$; if $Si O_3$ is accepted, the chloride of silicon. $Si Cl_3$, and the fluoride of silicon, $Si F_3$, and silicic ether, give three volumes of vapour; now, it is doubted whether the proportions of three volumes and six volumes exist at all, or that the vaporous molecule of compound bodies is ever divisible except by 2, 4, or 8. From this circumstance, and the analogy which subsists between silicic acid and titanic acid and binoxide of tin, the formula $Si O_2$ is adopted by many chemists, and, in consequence, the chloride, $Si Cl_2$, and the fluoride, $Si F_2$, and silicic ether possess, in the state of vapour, a molecule divisible by 2.

172. "Vapour densities may, at times, be made use of in research, as a means of ascertaining the nature of substances, where, from the small variation in their percentage composition, ultimate analysis becomes an unsafe guide. In examining the fluids produced by distillation of the Torbane-hill mineral, I obtained a series of homologous hydro-carbons, which only varied in composition as the boiling-point rose, by very small amounts,—so small indeed, that, notwithstanding the extreme care with which the analyses were made, it would have been unsafe to draw any conclusion as to the fractions to be selected as expressing the correct boiling-point from them alone; but, on the other hand, the densities of the vapours

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* According to Gerhardt's notation the atomic volume of compounds in the gaseous state is two volumes. (Consult par. 116.)

varied considerably with the different homologues, and by taking advantage of this fact I was enabled with perfect safety to pronounce not only on the formula of the substances, but also on their boiling-point.

173. "The vapour density not only enables us, with non-metallic elements, to pronounce upon the atomic weight, but also, taken in conjunction with the analysis of a compound with silver, upon the class of bodies among which it is to be grouped.

174. "For the purpose of determining the atomic weight of a substance, it is very desirable to obtain at least one compound that consists of one atom of each of its constituents. Now, it is possible to obtain silver-salts of most of the non-metallic elements, in which we are sure of the constitution being of the kind required. If, therefore, we analyze a salt of this description, we at once possess the data for determining its atomic weight. Let us suppose that a silver-salt has yielded

54·04 non-metallic element
45·96 silver
———
100·00

We say—

				At. wt. liq.		At. wt. non-metallic element.
45·96	:	54·04	::	108	:	126·98

175. "Now, on determining the density of its vapour, the non-metallic element gave 8·716; how are we to know to what class of bodies it belongs? A very little reflection will show, that as hydrogen is received as unity for atomic weights, if we received it also as unity for gaseous and vapour densities, the atomic weights of bodies of the same vapour volume would be expressed by their vapour density. It is obvious, then, that if a substance possesses the same vapour volume as hydrogen, its atomic weight will be obtained by dividing its vapour density by the density of hydrogen. If, therefore, the number obtained by dividing the vapour density of a non-metallic element by the density of hydrogen is identical with the number obtained by analysis of the silver-salt, it will be certain that the substance under examination possesses the same vapour volume as hydrogen, nitrogen, chlorine, &c. Let us try this in the present instance. The vapour density was, as

we have said, 8·716, and if we divide this by 0·0692, we obtain 125·95 as the result, which, although differing somewhat from 126·98, obtained as the atomic weight by analysing the silver-salt, is still quite a sufficient approximation to indicate that the body we have examined has a vapour volume the same as hydrogen. The body we have selected as an illustration is, as the student has probably perceived, iodine. If, on the other hand, it was necessary to divide the vapour-density by twice the density of hydrogen, to obtain the atomic weight, we may infer with safety that the vapour volume is that possessed by oxygen and elements of the same class."—*Greville Williams.*

CHAPTER III.

MOLECULAR ATOMS.*

Views hitherto held on the constitution of the elemental bodies, 176. *Mr. Brodie's views*, 177. *An even number of atoms of an element required in many chemical combinations*, 186. *Synthesis of particles of the same element in opposite polar conditions*, 187. *The molecular and elementary atoms possess different properties*, 191. *Allotropic modifications of the elements*, 192. *Brodie's views upon allotropism*, 192. *Nascent state of the elements*, 195. *Ozone and its formation*, 196. *The existence of molecular atoms of the compound radicals*, 197.

176. CHEMISTS have hitherto considered that chemical combination takes place only between unlike particles; that particles of the same nature are not influenced by the chemical, but only by the cohesive force. According to this view, no combination exists between the atoms of like bodies; they exist singly or detached. When, therefore, an element is liberated in the decomposition of compound bodies, its atoms are not supposed to enter into combination; and when an element enters into combination with other bodies, no decomposition of its molecules is supposed to take place.

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* The smallest quantity of an element which is supposed to be capable of existing in the free state. (See par. 120.)

177. Mr. Brodie, although not the first to question this view of the constitution of elementary bodies, was the first to establish, that at the moment of chemical change a chemical difference exists between the particles of which certain elemental bodies consist, perfectly the same in kind as that which exists between the particles of compound substances under similar circumstances, and on which the phenomena of combination and decomposition depend.

178. The proof, Mr. Brodie states, of the compound nature of a chemical substance is of a very simple kind. It lies in the fact, that it has been made by the combination of certain parts, or broken up into those parts, or at least in some phenomena which are supposed to be evidence of this. Indeed, the rational formula of a chemical substance is but a memorandum of its re-actions, and a particular mode of expressing the law of the synthesis and analysis of the body, apart from which it has but little meaning. The true nature, therefore, and chemical formula of the elemental bodies, as of all other substances, is to be discovered by the study of the series of chemical changes in which they are formed, and by the phenomena which they present when they pass into the combined condition. There are even well-known facts of great importance in this point of view, some unexplained, and some, I conceive, misinterpreted.

179. "The point which I shall seek to establish is this, —that, at the moment of chemical change, a chemical difference exists between the particles of which certain elemental bodies consist, perfectly the same in kind to that which exists between the particles of compound substances under similar circumstances, and on which the phenomena of combination and decomposition depend. That a peculiar chemical relation exists between two particles which combine, is generally admitted and expressed by the term affinity. The electro-chemical theory has defined more exactly in what this affinity consists, and states that the two particles are to one another in a positive and negative electric relation.* But I do not know that it has ever been pointed out that this chemical relation—this

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* After the student has become thoroughly conversant with this chapter, he ought to study the section on Chemical Polarity in Graham's "Elements of Chemistry," vol. i., 2nd edit.

affinity between the particles of a substance—is an essential condition of the decomposition as well as of the composition of the body. As I am about to infer a chemical difference between the particles of the element from the fact of their chemical separation, I must say a few words upon this point, and I shall simplify the whole question by stating briefly the mode in which I consider chemical change to be effected. I may do this sufficiently for my present purpose in the following propositions:—

"1. That when two particles chemically combine, a certain chemical relation exists between them, which is expressed by the terms *positive* and *negative*. The chemical difference of the particles I term the difference between their conditions in this respect.

"2. That when chemical combination takes place between the particles of which any two or more substances consist, a chemical difference exists between the particles of each substance, so that the particles of the same substance are to one another in a positive and negative relation.

"3. That the chemical relation between any two particles of these substances is determined by the chemical relation of all the other particles with which they are for the time being associated. Substances, the particles of which are to one another in this peculiar chemical relation, I term chemically polar.

180. "Silver cannot be oxidized by the direct action of oxygen on the metal, but oxide of silver is readily formed by boiling the chloride of this metal with potash. The particles of oxygen and silver have, therefore, acquired by this association with the chlorine and potassium a chemical relation or affinity, which at other times they have not. This is the fact. The rational conception of the fact is given in the expression,—

$$\overset{+}{\mathrm{Ag}}\;\overset{-}{\mathrm{Cl}}\;\overset{+}{\mathrm{K}}\;\overset{-}{\mathrm{O}} = \mathrm{Ag\,O} + \mathrm{K\,Cl},$$

in which I have indicated the polar relation of the substances. The chemical relation, therefore, between the oxygen and silver is essentially dependent on the chemical relation between the oxygen and potassium, in the same way as a negative and positive electricity are related to each other. The same is true of the relation between any other two particles of the system. Hence chemical decomposition is an essential condition of chemical combination; so that when we see one of these events we may infer the other.

181. "On the other hand, where this polar division of the substance cannot take place, there is no chemical action, or, at any rate, it takes place with greater difficulty: thus, anhydrous sulphuric acid may be distilled off carbonate of potash without alteration; and generally, the so-called anhydrous acids have none of the combining properties of the hydrates to which they correspond; the reason of this being, that when these bodies combine they do not decompose, and that it is by the very fact alone of the decomposition of the substance, that the combining power is developed in the particles of which they consist, so that in the chemical change which is thus represented,—

$$\overset{+}{H}\,\overset{-}{SO_4}\;\overset{+}{K}\overset{-}{O} = HO + SO_4K,$$

the two combinations which take place are not two combinations accidentally simultaneous, but correlative and mutually dependent phenomena, which we cannot separate.

182. "In the case of double decomposition, each of the four substances which enter into the change is combined; but it does not appear that this state of combination is necessary to the action. It can take place, also, and in the same manner, when the combining substances are only in contact with each other, and not in combination, provided always that there is the right chemical difference between them, which, however, is essential. Thus, for example, when iodine and phosphorus decompose water (in the usual mode of the formation of hydriodic acid), the chemical relation between the iodine and phosphorus is an essential condition of the action. The same remark applies to the decomposition of water between nitric oxide and chlorine, which can be effected by neither body separately; so that the changes which take place in these experiments are not simply due to the fact that the chlorine or iodine stand in one relation to water, or to the elements of water, and the nitric oxide or phosphorus in another, and that thus the water breaks up, being acted upon by two opposite forces; but that there is also, and must be, a certain chemical difference between the chlorine and nitric oxide, and between the iodine and phosphorus, which

is as essential and important a condition to the propagation of the action, as their relation to the water itself, and indeed, without which, they could not have this relation. I am not aware this remark has before been made, nor do I think it likely that it should have been made, but upon the view which I have given, of which it is a consequence.

183. "Facts corresponding to these cases of composition are to be observed, as might be expected, in the decomposition of bodies; for if decomposition be the condition of combination, so, of course, must combination be the condition of decomposition.

184. "On the view which I have here given of the nature of chemical change, the very existence of the elemental bodies was a strange and unaccountable anomaly. I have regarded the molecular structure of bodies but as an expression of the law of their synthesis and analysis, and this law again as a result of the peculiar nature of chemical force. It was, therefore, truly difficult to conceive how an element, in the sense of Berzelius,* was formed. The formation of this 'uncombined particle' was a fact quite different to the formation of a compound substance, and yet it seemed as unreasonable to suppose that the laws of chemical action should vary in different materials, as that the laws of motion should be different in different bodies. I therefore considered attentively, what we really knew of the laws of chemical change in these bodies. Examples occurred to me, both of the chemical division and chemical synthesis of the elements, by which various phenomena, hitherto obscure, might be explained. The experiments of the first class prove that a division of the elemental bodies, which is known to occur in certain cases of chemical change, is truly a chemical and not simply a mechanical division of these substances. This is shown by the fact that the particles of the element thus separated show the peculiar combining properties of 'nascent bodies.' It is not necessary to my argument that the precise view which I have given of the nature of this 'nascent state' should be admitted; provided only it be allowed, that these properties depend upon the fact

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* The atoms of an elementary body do not possess any force of mutual combination: they adhere together only by virtue of the force of aggregation.—*Berzelius.*

that the particle is issuing from a state of combination, which is generally allowed."[*]

185. The above extracts from the "Memoir on Chemical Change" are sufficient to make the student acquainted with Mr. Brodie's views upon this subject. We will now arrange the facts into three classes, which appear to prove that the atoms of the elements, in their free state, *are united in pairs.*

186. 1*st Class.*—In a great many of the chemical combinations in which *an element* is one of the combining bodies, an even number of atoms of the element is required. The atoms of the elements appear, therefore, to be associated in *binary groups.* Examples:—

1. When chlorine acts upon potash, two compounds are always formed. The following is the reaction when hypochlorite of potash is produced:—

$$2\,KO + Cl\,Cl = KO,\ Cl\,O + K\,Cl.$$[†]

When chlorate of potash is formed, the following reaction takes place:—

$$6\,KO + 3\,Cl\,Cl = 5\,K\,Cl + KO,\ Cl\,O_5.$$[‡]

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[*] Brodie "On the Condition of Certain Elements at the Moment of Chemical Change."—*Phil. Trans.*, part ii. 1850.

[†] The chemical change recorded above corresponds in every respect with the following:—

$$2\,KO + Cy\,Cl = K\,O,\ Cy\,O + K\,Cl.$$

[‡] Laurent, in his "Chemical Method," recommends that when substitutional reactions are represented in the form of an equation, the second member of the equation should be written underneath the first. This is a very excellent plan, for we at once perceive, when the equation is written in this manner, that to each term of the superior member there is a corresponding term in the inferior one, as shown in the following examples. The examples are written according to the new views, and with the new atomic weights:—

1st.—Action of chlorine upon hydrogen - - - - $\left\{\begin{array}{l} Cl\,Cl + H\,H = \\ H\,Cl + H\,Cl. \end{array}\right.$

2nd.—Chlorine upon hydrate of potash - - - - $\left\{\begin{array}{l} Cl\,Cl + K\,H\,O + K\,H\,O = \\ K\,Cl + K\,Cl\,O + H\,H\,O. \end{array}\right.$

3rd.—Chlorine upon hydrate of potash - - - - $\left\{\begin{array}{l} 3\,Cl\,Cl + 2\,K\,H\,O + K\,H\,O + 3\,K\,H\,O = \\ 3\,K\,Cl + 2\,K\,Cl + K\,Cl\,O_3 + 3\,H\,H\,O. \end{array}\right.$

4th.—Action of chlorine and iodine on water - - $\left\{\begin{array}{l} 5\,Cl\,Cl + 5\,H\,H\,O + H\,H\,O + I\,I = \\ 5\,H\,Cl + 5\,H\,Cl + H\,I\,O_3 + H\,I\,O_3. \end{array}\right.$

5th.—Sulphuric acid upon peroxide of manganese - $\left\{\begin{array}{l} H_2\,S\,O_4 + Mn_2\,O_2 = \\ Mn_2\,S\,O_4 + H_2\,O + O. \end{array}\right.$

6th.—Sulphuric acid upon carbonate of potash - $\left\{\begin{array}{l} H_2\,S\,O_4 + K_2\,C\,O_3 = \\ K_2\,S\,O_4 + C\,O_2 + H_2\,O. \end{array}\right.$

7th.—Chloride of benzoyl upon water - - - - $\left\{\begin{array}{l} C_7\,H_5\,Cl\,O + H_2\,O = \\ C_7\,H_6\,O_2 + H\,Cl. \end{array}\right.$

2. "There does not exist a single organic compound upon which we can effect any reaction by employing an uneven number of atoms of chlorine. In every case it is Cl_2, or a multiple thereof, which determines the reaction. A body *can contain an uneven number* of atoms of chlorine; but in order to form it, we must employ an *even number* of atoms. The following are a few examples of this statement."—*Laurent.*

Etherin - - $C_2H_2 + Cl\,Cl = C_2H\,Cl + H\,Cl$
Propylene - $C_6H_6 + Cl\,Cl = C_6H_5\,Cl + H\,Cl$
„ - $C_6H_6 + 2Cl\,Cl = C_6H_4\,Cl_2 + 2H\,Cl$
„ - $C_6H_6 + 6Cl\,Cl = C_6\,Cl_6 + 6H\,Cl$

3. When sulphur is fused at a gentle heat with an alkaline hydrate, or boiled with an aqueous solution of the alkali, two compounds, pentasulphide of potassium and hyposulphite of potash, are formed:—

$$3\,K\,O + 6\,S\,S = K\,O,\,S_2\,O_2 + 2\,K\,S_5.$$

4. When metallic sulphides oxidize in the air, both elements enter into combination with the oxygen; thus,—

$$Ni\,S + 2\,O\,O = Ni\,O,\,S\,O_3.$$

187. *2nd Class.*—There are a great number of decompositions which cannot be explained in any satisfactory manner, in my opinion, unless we admit that the atoms of the same element are capable of entering into combination with each other. Examples:—

1. When a solution of bichromate of potash is poured into a strong and acid solution of the peroxide of barium in hydrochloric or nitric acid, a violent effervescence and escape of oxygen takes place: apart, these solutions are perfectly stable; bring them together, they are both decomposed; the chromic acid passes into chloride of chromium, the peroxide of hydrogen into water, and the oxygen formed is due to the simultaneous decomposition of both bodies; thus,—

$$3\,H\,Cl + 2\,Cr\,O_3 + 3\,H\,O_2 = Cr_2\,Cl_3 + 6\,H\,O + 3\,O\,O.$$

Brodie regards the oxygen itself in this experiment as

—In the fifth reaction, peroxide of hydrogen ought to be formed: but this body, not being capable of existing in the presence of binoxide of manganese, undergoes decomposition, and sets free its oxygen, whence the interference with the symmetry of the reaction.

In the sixth reaction, the symmetry is destroyed, because $H_2\,C\,O_3$ being, under ordinary circumstances, incapable of existing, becomes decomposed immediately into $H_2\,O$ and $C\,O_2$.

the true reducing agent; he believes that the chromic acid is decomposed by the oxygen of the peroxide of hydrogen, according to the same law of decomposition, and for the very same reason, as it would be by hydrogen itself if a piece of zinc were thrown into the acid solution, this reason being the polarity of the particles induced by chemical change.*

2. Hydride of copper, Cu_2H in contact with strong hydrochloric acid, is decomposed along with the acid, chloride of copper, Cu_2Cl, being formed, and hydrogen evolved; thus,—

$$\overset{+}{Cu_2}\,\overset{-}{H} + \overset{+}{H}\,\overset{-}{Cl} = Cu_2\,Cl + H\,H.$$

This is perfectly analogous to the following decomposition:—

$$\overset{+}{Cu_2}\,\overset{-}{O} + \overset{+}{H}\,\overset{-}{Cl} = Cu_2\,O + H\,O.$$

Hydrochloric acid scarcely acts upon copper; the combination of hydrogen with copper, far from favouring the action of the acid upon the metal, ought, according to the received ideas, to add a new obstacle to it. Hydrochloric acid also dissolves an alloy of copper and zinc, although on the copper itself it has no action. The hydride of copper is itself, in its chemical relations, an alloy; the action of the acid consequently is the same upon the compound of copper and hydrogen as upon the compound of copper and zinc, and the explanation of these facts involves similar phenomena. Thus,—

$$\overset{+}{H}\,\overset{-}{Cl}\,\overset{+}{Zn}\,\overset{-}{Cu}\,\overset{+}{Cl}\,\overset{-}{H} = Zn\,Cl + Cu\,Cl + H\,H.$$

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* The decomposition of a compound by heat is explained by Brodie in the same way; thus,—

$$2HgO = Hg\,Hg + O\,O.$$

"In certain cases we can trace the very mode in which this decomposition by heat takes place. Thus, in the decomposition of chlorate of potash by heat, the true way in which this substance is decomposed is, as discovered by Serullas, the decomposition of one particle by the next. The chlorate is first oxidized to perchlorate, and this perchlorate, as shown by Millon, again reduced to chlorate, with evolution of oxygen. Thus the action proceeds by a continual oxidation and reduction of the substance, the phenomena being very similar to the oxidation of the chromic acid by the peroxide of hydrogen, and the spontaneous decomposition of the compound formed. By mixing chlorate of potash with oxide of copper, the formation of the perchlorate is entirely prevented, and the action converted into one of spontaneous decomposition."

Brodie explains in a similar way the oxidation and solution of platinum in nitric acid when alloyed with silver. Platinum by itself, as is well known, will not oxidate and dissolve in the acid.

3. When iodine is added to peroxide of barium, the following changes take place:—

$$2\,Ba\,O_2 + I = 2\,Ba\,I + 2\,O\,O.$$

We add the two following chemical changes, in order that the student may contrast the three:—

$$(1).\ I\,I + Ba\,O = Ba\,I + I\,O.$$
$$(2).\ I\,P + Ba\,O = Ba\,I + P\,O.$$

188. The oxides of gold, silver, and mercury, on being placed in a solution of peroxide of hydrogen,* decompose, and are decomposed by, that body, although *apart* the peroxide and the metallic oxides are perfectly stable; the metallic oxides lose the whole of their oxygen, whilst the peroxide loses one-half, and thus becomes converted into water. "The simultaneous reduction of the peroxide of hydrogen and the oxide of silver is a solitary fact, by the side of which chemists have been able to place scarcely an analogous, much less a similar instance. Hitherto, in the breaking up of the oxide of silver and the peroxide of hydrogen, no chemical fact has been recognised but the simultaneous decomposition of two chemical substances. This is that fact for which it has been so difficult to account. Were it, for example, a hydride of silver which was thus decomposed, and water formed and not simply oxygen, the experiment would have attracted no attention. On the view I have given, the formation of the oxygen itself is as truly a chemical synthesis as the formation of water, and may be substituted for it in a chemical change. This supplies an explanation of these facts at once adequate and simple; the oxide of silver in this experiment being reduced by the oxygen of the peroxide of hydrogen, just as in other cases it might be by hydrogen; the formation of the silver from the particles of which it is composed being the corresponding fact in the decomposition of the oxide of silver to the formation

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* Instead of employing peroxide of hydrogen, which is troublesome to prepare, the decomposition can be shown by employing a solution of peroxide of barium in hydrochloric or acetic acid.

of water in the peroxide, so that we may represent the change thus:—

$$\underbrace{\overset{+}{H}\,\overset{-}{O}\,\overset{+}{O}\,\overset{-}{O}\,\overset{+}{Ag_{\frac{1}{2}}}\,\overset{-}{Ag_{\frac{1}{2}}}} = H\,O + O_2 + Ag.^{*}$$

188. "No one can be more sensible than I am of the wide interval which exists between such a mode of representing a chemical change and an ascertained fact. The very form in which I have just expressed the decomposition involves an important assumption; an assumption indeed on which, in my opinion, the whole question rests. If it be true that these bodies are thus decomposed in definite and equivalent proportions, and that the simultaneous decomposition of the bodies proceeds according to this law, it is impossible to deny the chemical relation of these changes and the mutual chemical action of the substances; and, on the other hand, if the formation of this oxygen is to be regarded as a true chemical synthesis, this synthesis must follow the universal law of the formation of chemical substances, and the masses must combine in definite and equivalent proportions. It was, therefore, the quantitative relation of the decomposing substances which seemed to me the essential point to be determined, and which experiment alone could decide; for it was quite possible (and indeed had to be taken for granted) that the action varied according to some other law. It might have none of the characters of a chemical change; it might, for example, vary directly with the acting masses, or with the temperature alone, or be a function, so to say, of so many variables that the true law of action would be altogether hidden."—*Brodie.*

190. Wurtz found that an equivalent of hydrochloric acid exactly decomposed an equivalent of hydride of copper (187-2); Brodie also found that an equivalent of iodine always exactly decomposed an equivalent of peroxide of barium, if the latter were perfectly pure (187-3); but in the decomposition of other substances with peroxide of barium, Brodie found that the proportions in which the

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* Berzelius and other chemical philosophers have ascribed decompositions of this kind to a new power, which they term the *Catalytic force*, and the effect of the action of this force they term *Catalysis*, or decomposition by contact. The student is referred to the larger works on chemistry for further information about Catalysis, and also to a paper on that subject, by Dr. Playfair, in the "Proceedings of the Chemical Society."

substances were decomposed varied with the nature of the chemical substances reduced, with the temperature, with the mass, and also with the strength of the solution.*

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* For a further account of these experiments, the student is referred to the seventh volume of the "Chemical Society's Journal."

During the time this work was passing through the press, Mr. Brodie communicated to the Royal Society the following important note on the oxidation and disoxidation effected by peroxide of hydrogen:—"In a former communication I laid before the Society a detailed investigation as to the remarkable disoxidation of certain metallic oxides (of which the decomposition of the oxide of silver may be regarded as typical) by the peroxide of hydrogen. I suggested that this decomposition was of a simple and normal character; that the element oxygen was formed according to a molecular law, identical with that according to which compound substances are formed: and that the mutual decomposition of the two oxides was determined by the synthesis of the particles of oxygen in opposite polar conditions, according to the equation,—

$$Ag_2\,O + H_2\,O_2 = Ag_2 + H_2\,O + O^2$$

"After an interval of nearly ten years this explanation, together with various facts bearing upon the theory of this action, and which were given for the first time in the paper alluded to, have been reproduced as original discoveries by Schönbein.

"The reaction does not, however, present itself under this simple form. The amount of oxygen lost by the oxide of silver is a variable quantity, comprised between the extreme limits of the catalytic action, in which the reduction is zero, and the normal chemical action, as expressed in the above equation. The reason for this variation is to be sought in the disturbing influence of the metal formed during the decomposition.

"It is my intention shortly to communicate to the Society a prosecution of the above inquiry, in which I investigate the decomposition, by the peroxide of hydrogen, of certain oxygenated substances contained in solution, where the perturbing causes, which affect the decomposition of the solid oxides, and conceal the simplicity of the reaction, do not exist.

"The methods by which the following results have been obtained will hereafter be given in detail. I confine myself merely to a brief *résumé* of the conclusions:—

"(1). When an acid solution of permanganic acid is decomposed by peroxide of hydrogen, the decomposition is in an invariable atomic proportion, according to the equation,—

$$Mn_4\,O_7 + 5\,H_2\,O_2 = 2\,Mn_2\,O + 5\,H_2\,O + 5\,O_2.$$

"(2). An alkaline solution of ferricyanide of potassium is reduced by the peroxide of barium to ferrocyanide, with the evolution of two atoms of oxygen; thus,—

$$2\,K_3\,Fe_2\,Cy_6 + 2\,K\,H\,O + Ba_2\,O_2 = 2\,K_4\,Fe_2\,Cy_6 + 2\,Ba\,H\,O + O_2.$$

"(3). An alkaline solution of hypochlorite of barium is reduced by the peroxide of barium, according to the equation,—

$$Ba\,Cl\,O + Ba_2\,O_2 + H_2\,O = Ba\,Cl + 2\,Ba\,H\,O + O_2.$$

"A similar change takes place, as might be anticipated, with an aqueous solution of chlorine in the acid solution of peroxide of barium, but more slowly.

"(4). The decomposition of chromic acid is of special interest. In this case there are two distinct reactions, the first of which takes place when chromic acid is in excess, according to the equation,—

$$2\,Cr_2\,O_3 + 3\,H_2\,O_2 = Cr_4\,O_3 + 3\,H_2\,O + 3\,O_2;$$

191. *3rd Class.*—As a chemical compound possesses properties perfectly different from those of its constituents, it follows, that if two or more atoms of the same element are capable of entering into combination, the homogeneous compound,* and the elementary atoms in their free state, will be distinguished by a difference in

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the second, which occurs when a large excess of peroxide of hydrogen is present, and in which the peroxide of hydrogen loses exactly double the amount of oxygen lost by the chromic acid, so that the final result is expressed by the equation—,

$$2\,Cr_2\,O_3 + 6\,H_2\,O_2 = Cr_4\,O_3 + 6\,H_2\,O + O_9.$$

"In the intervals between these reactions, the ratio of the loss of oxygen from the peroxide to the loss from the chromic acid, varies between the limits 1 and 2 according to a definite law, being proportional to the ratio of the masses of the substances employed. I am able to show, by direct experiment, that the reaction between the extreme limits is the sum of two distinct and simple atomic decompositions.

"The alkaline peroxides which produce these peculiar effects of reduction, under other conditions act as powerful oxidizing agents; thus an acid solution of hydrated protoxide of manganese is oxidized by peroxide of barium to the condition of peroxide of manganese. A concentrated solution of hydrochloric acid evolves chlorine from peroxide of barium.

"This last reaction I have made the subject of a special investigation, with the view of determining the conditions under which the two reactions—

$$4\,H\,Cl + Ba_2\,O_2 = 2\,Ba\,Cl + 2\,H_2\,O + Cl_2,$$

and

$$2\,H\,Cl + Ba_2\,O_2 = 2\,Ba\,Cl + H_2\,O_2,$$

respectively take place; and I find that when a solution of hydrochloric acid is boiled with peroxide of barium, if the solution be concentrated, chlorine—if the solution be dilute, oxygen—exclusively is evolved; and that for each intermediate degree of dilution chlorine and oxygen together are evolved in a constant ratio.

"It is thus seen that those differences in the behaviour of the different classes of peroxides, from which an imaginary distinction has been drawn between the oxygen respectively contained in them as positive or negative,† are not fundamental and characteristic differences. The oxygen in the peroxide of barium is the same as that in the peroxide of manganese, according to the only test of identity which we can apply, for we can produce with it the same effects. Nor are the peculiarities in the reactions of the oxygen of the alkaline peroxides of such a nature as to need any special hypothesis to account for them; for in no case are the combining properties of the particles of matter, like their atomic weights, constant for each chemical substance, but they are variable properties, depending on the physical conditions in which the particles are placed, and the chemical substances with which they are associated.

* We shall call compounds consisting of a combination of the atoms of the same element, *homogeneous compounds*, to distinguish them from compounds composed of unlike elements: the latter class of compounds, composed of unlike elements, we shall call *heterogeneous compounds*.

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† Schönbein has drawn a distinction, and this is evidently an allusion to his view.—R. G.

their properties; that the elements do not possess under all circumstances the same physical and chemical properties, but that the same element differs as much in properties under different conditions as some heterogeneous compounds differ from *their* constituents is evidenced by the allotropic modifications of some of the elements,* and by the *nascent*, compared with the *ordinary*, *state* of the elements.

192. To show the student that the properties vary with the conditions of the element, we will first of all contrast the properties possessed by phosphorus, by sulphur, and by carbon, in the different conditions in which each of these elements is capable of existing. Phosphorus can be obtained in the crystalline, vitreous, and amorphous state. In its ordinary state, it is a soft, semi-transparent, colourless, waxy-looking solid, which fumes in the air, emitting white vapours of an alliaceous odour. Its specific gravity is 1·83. It fuses at 111·5° F. It is very inflammable; it takes fire in the open air a few degrees above its fusing point. The crystalline form is equally inflammable with the vitreous. Amorphous phosphorus is red. In this state it is insoluble in a great many liquids in which the crystalline and waxy forms dissolve. The density of red phosphorus is 2·14. It has no smell; and it may be heated in the open air, without change, until the temperature reaches 500° F.: at this heat it melts, and bursts into flame. One form of sulphur has a density of 2·05, and melts at 239° F.; another form of the element has a density of 1·98, and melts at 248° F.; and a third form has a density of 1·957. These three varieties of sulphur are also distinguished from each other by a difference in some of their other properties. The student has only to contrast the properties of the diamond,

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* "There appear to be four different conditions in which solid bodies may exist. They may be—1st. *Crystalline*, as diamond, garnet, felspars. 2nd. *Vitreous*, or glassy, as glass itself, transparent arsenious acid, and barley sugar. 3rd. *Amorphous*, or destitute of crystalline form altogether, as tinder, chalk, or clay. 4th. *Organized*, or arranged in masses, consisting of cells, fibres, or membranes, like the tissues of animals or vegetables, as hair, muscle, skin, wood, bark, leaves, &c."—*Miller*.

Some of the simple bodies can exist in different forms, and in the different forms the same elements possess different properties; these different forms have been called the allotropic states of the element. The word *allotropy* is derived from two Greek words, signifying a different manner or nature. It is probable that all the elements can exist in two or more different forms.

graphite (the black-lead of pencils), and ordinary charcoal, to see that the properties of carbon are as various as the conditions in which it can exist. Brodie has endeavoured to ascertain experimentally whether the allotropic differences of the elements are to be regarded as purely physical, or as chemical differences of matter. "For if it were proved that the formation of the element is a chemical synthesis of the same nature as the formation of a compound substance, we are enabled to transfer to the element those ideas of *form* by which we most reasonably explain isomeric differences,* and to comprehend that, in their case also, two or more substances may exist, identical in their ultimate chemical constitution, yet differing in the arrangement of their particles." Brodie reasoned that, if the allotropic differences were due to chemical differences, then different allotropic forms must exhibit different chemical reactions; and it might be anticipated, as not improbable, that these different forms might even enter into combination with different combining weights. Brodie was led to believe, from the differences which charcoal obtained from sugar, and which graphite displayed when treated with concentrated sulphuric acid and chlorate of potash, that graphite is a peculiar compound of carbon. He then treated graphite with a mixture of nitric acid and chlorate of potash, and he obtained, after treating the substance four or five times with these re-agents, and washing and drying the substance after each treatment, a substance having the formula $-\!\!\!\!\mathrm{C}_{11}\,\mathrm{H}_4\,-\!\!\!\!\mathrm{O}_3$,† which he calls "graphic acid." When graphic acid is heated to 520° F., with proper precautions, it is decomposed, carbonic acid and water are given off, and a substance having a graphitoid appearance is left, having the formula $-\!\!\!\!\mathrm{C}_{22}\,\mathrm{H}_2\,-\!\!\!\!\mathrm{O}_4$; and when this substance is heated, in an atmosphere of nitrogen, to a temperature of 480° F., it is decomposed, water and carbonic oxide are given off, and a substance is left having the formula $-\!\!\!\!\mathrm{C}_{66}\,\mathrm{H}_4\,-\!\!\!\!\mathrm{O}_{11}$.

193. Brodie considers that in these compounds the

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* For a description of Isomerism, see the author's "First Step in Chemistry," 3rd edition, page 199.

† The double atoms of oxygen, sulphur, carbon, selenium, or tellurium are sometimes distinguished by drawing a line through the letter or symbol, as in the present case.

graphite retains its allotropic state, which he terms *Graphon*, and that it possesses in this form a combining number of 33, for the following reasons:—Buff and Wöhler recently discovered a remarkable series of compounds derived from the graphitoidal form of silicon,* among which is a compound of silicon, hydrogen, and oxygen, of the formula $Si_4\ H_4\ O_5$. The properties of this substance correspond very closely with those of graphic acid; it is, therefore, a reasonable inference that the graphite compound is the same term in the system of carbon, as the silicon compound in the system of silicon. When this analogy is stated in the formula of the substance, we are led to very remarkable conclusions. The total weight of graphite which in the compound is combined with four atoms of hydrogen, and five of oxygen, is 132. If we assume this weight is, like the corresponding weight, 84 of silicon, to be divided into four parts, we arrive at the number 33, as the atomic weight of graphite. Representing this weight by the letters Gr, the formulæ of the substances $\text{Ꞓ}_{11}\ H_4\ \text{Ɵ}_5$, $\text{Ꞓ}_{22}\ H_2\ \text{Ɵ}_4$, and $\text{Ꞓ}_{66}\ H_4\ \text{Ɵ}_{11}$, become $Gr_4\ H_4\ \text{Ɵ}_5$, $Gr_8\ H_2\ \text{Ɵ}_4$, and $Gr_{24}\ H_4\ \text{Ɵ}_{11}$. Brodie believes that this view of the atomic weight of graphite is supported by its specific heat; and he also thinks that the relation which exists between the atomic weights of boron, silicon, and zircon, and that form of carbon for which a place may be claimed as a distinct element, *graphon*, is precisely the kind of numerical relation† which is found to exist between the weights of analogous elements. We have—

Boron - - - - - -	11
Silicon - - - - - -	21
Graphon - - - - -	33
Zircon - - - - - -	66

194. "These considerations lead to the remarkable inference that carbon, in the form of graphite, functions as a distinct element; that it forms a distinct system of

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* Silicon can be obtained in three distinct modifications, viz.—the *amorphous*, Si γ, the *graphitoid*, Si β, and the *crystalline*, Si α, modification. For further information on silicon and its compounds, the student is referred to Miller's "Inorganic Chemistry," the second edition of vol. ii.

† The question of specific heat and numerical relation will be explained in some of the following chapters.

combinations, into which it enters with a distinct atomic weight—the weight, 33. Analogy would lead us to a similar conclusion with regard to the elements boron and silicon. How far this inference is to be extended to the allotropic forms of other elements, experiment alone can decide." *

195. The affinities of the elements in *their nascent state* are much more powerful than in the ordinary state of the elements; nitrogen, for instance, cannot, except with very great difficulty, be made to unite directly with any element, but requires for its combination that one or both the elements should be in the nascent state; in order to effect the combination of chlorine and hydrogen, oxygen and hydrogen, independently of any agent, such as heat, it is necessary to bring them together in their nascent state. To effect the union of a solid with a gaseous body, it is necessary in a number of cases to bring them together in their nascent state; thus, no chemical combination will take place if a stream of hydrogen be passed into sulphur. If, however, the two elements are set free from other combinations at the same moment and in presence of one another, they combine together and form hydrosulphuric acid. This is also the case with hydrogen and the following substances:—phosphorus, carbon, arsenic, antimony, &c. We cannot well explain why the affinities of the elements should be so much greater at the *moment* they are set free from their (heterogeneous) combinations than they are afterwards, unless we admit that the atoms of the same elements are capable of entering into combination. If we admit the existence of molecular atoms, then there is no difficulty in accounting for the great disparity in the affinities of the elements in the two states; for in the nascent state the atoms of the element are *uncombined*, in the ordinary state they are united; consequently, when two elements are set free from other combinations at the same moment and in presence of each other, the two elements enter into combination, because the *unlike* atoms have a greater affinity for each other than the *like* atoms have; or, as it would be expressed on Mr. Brodie's theory, the unlike

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* Brodie "On the Atomic Weight of Graphite:" *Chemical Society's Journal*, vol. xii.

atoms are in a greater positive and negative relation. But if we bring the elements in their ordinary state together they will not combine, or at least they will combine with greater difficulty than they would if they were in the nascent state, because the affinity of the like atoms, now that the atoms of the elements are in a state of combination, is sufficient to prevent combination taking place between the unlike atoms; but just as double decomposition may be effected by the aid of heat, or some other agent, between two heterogeneous compounds which unassisted cannot mutually decompose one another, so two homogeneous compounds which cannot undergo decomposition of themselves, and so form two heterogeneous compounds, may by the aid of heat, or some other agent, undergo this chemical change. Examples.—If carbonate of lime ($Ca\,O, C\,O_2$) and chloride of ammonium ($N\,H_4\,Cl$) be added together, no chemical change will ensue, unless they are exposed to a temperature higher than 212° F.; in that case they will mutually decompose each other, carbonate of ammonia ($N\,H_4\,O, C\,O_2$) and chloride of calcium ($Ca\,Cl$) being formed. If hydrogen ($H\,H$) and chlorine ($Cl\,Cl$) are added together, no chemical change takes place unless heat, electricity (which acts by the heat it produces), or light be applied; by the aid of one or other of these agents, the $H\,H$ and $Cl\,Cl$ are mutually decomposed, and two atoms of $H\,Cl$ are formed; but if H and Cl are brought together, as is the case when they are in the nascent state, then the two elements unite and form hydrochloric acid without the aid of any agent.

196. The singular body ozone, which at one time was supposed to be a teroxide of hydrogen, but which is now generally regarded as oxygen in a very active state, is obtained by transmitting a succession of electric sparks through air or dry oxygen. It can also be formed by placing a clean stick of phosphorus, moistened with a few drops of water, in a bottle of atmospheric air; the phosphorus is slowly oxidized, and the formation of ozone accompanies the oxidation. It is also stated, that the oxygen which is evolved from peroxide of barium on the addition of sulphuric acid, contains ozone. The mode of its formation, especially by phosphorus, appears strongly to corroborate not only the binary association of

the elements, but also that the combined atoms are in two oppositely polarized forms.[*]

197. We have now to show that the atoms of the compound radicals[†] of the ethers *unite* when they are separated from heterogeneous combinations; it is therefore highly probable, that the atoms of all compound bodies which play the same part as elementary bodies cannot exist in a state of isolation; that they are, when not forming constituents of heterogeneous compounds, united in binary groups forming homogeneous compounds.

198. Frankland[‡] isolated the radical ethyl by acting upon iodide of ethyl ($C_4 H_5 I$) with zinc in sealed tubes; he found that along with ethyl and iodide of zinc, there was formed a compound of zinc and ethyl having this formula, $C_4 H_5 Zn$, which he named zinc ethyl, and besides the ethyl, two other compounds of carbon and hydrogen, having the formula $C_4 H_4$ and $C_4 H_6$: each of these compounds of carbon and hydrogen, the ethyl and the other two, belong to a distinct group of the large family of hydro-carbons. As zinc ethyl is decomposed by water, Frankland found that when water was present along with the iodide of ethyl and zinc the decomposition was different, not only was there no zinc ethyl present, but there was only one hydro-carbon $C_4 H_6$, and instead of iodide of zinc ($Zn I$) oxyiodide of zinc ($Zn O, Zn I$) was the iodine compound of zinc that was formed; the following changes therefore take place when water is present:—

$$C_4 H_5 I + 2 Zn + H O = C_4 H_6 + Zn O, Zn I.$$

199. Ethyl possesses the closest chemical relationship with hydrogen; in all its combinations it stands in the same relation to the other constituents of its different compounds as hydrogen does when it is united with

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[*] The student is referred to the "Philosophical Magazine," for 1858, and subsequent volumes, for a description of Schönbein's speculations upon the existence of two opposite forms of oxygen; and to the "Philosophical Transactions," for Andrews's views on the constitution of ozone.

[†] A name applied to any compound which is capable of combining with simple bodies.

[‡] We strongly recommend the student to study the beautiful researches of Frankland, on the isolation of the alcohol radicals, in the early volumes of the "Journal of the Chemical Society of London."

Many of the other alcohol radicals have been isolated, and the same reasoning applies to them as to ethyl.

them; if, therefore, we represent the compound of chlorine and hydrogen by the formula $H\,Cl$, and hydrogen itself by the symbol H, we must represent the compound of chlorine and ethyl by the formula $C_4\,H_5\,Cl$, and ethyl itself by the formula $C_4\,H_5$; this was the formula assigned to ethyl by Frankland: according to this formula, the ethyl atom forms only one volume of vapour. Zinc ethyl ($C_4\,H_5\,Zn$) is decomposed, as we have already stated, by water, oxide of zinc, and a hydro-carbon, which may be represented by the empirical formula $C_4\,H_6$, being formed. Frankland considered, that in the decomposition of the zinc ethyl by water, the zinc in the ethyl compound was displaced by hydrogen: the rational formula of the hydro-carbon must therefore be $C_4\,H_5\,H$, a compound of ethyl and hydrogen in equal atomic proportions; this compound he has called hydride of ethyl. The rational formula of the hydro-carbon, which is formed by the action of zinc upon iodide of ethyl in the presence of water, and which we have represented by the empirical formula $C_4\,H_6$, must be $C_4\,H_5\,H$,[*] as it is the same body as that formed by the action of water upon zinc ethyl. The hydride of ethyl atom forms two volumes of vapour; it contains one volume of ethyl vapour, and one volume of hydrogen, united without condensation.

200. The formula $C_4\,H_5$ for ethyl, and the corresponding formulæ for the other alcohol radicals, involved the singular anomaly that the atom of these bodies would only form one volume of vapour, whereas all other known hydro-carbons occupied two volumes;[†] Gerhardt, therefore, proposed to double the formulæ, in order to make their vapour volume correspond to all other hydro-carbons; for the expression $C_8\,H_{10}$ for ethyl, and a corresponding expression for the other radicals, corresponds, like all other hydro-carbons, to two volumes of vapour. Hofmann likewise thought the formulæ ought to be doubled, and for the following reasons:—

201. 1st.—The volumes of the vapour of the alcohol

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[*] This body was first obtained by Kolbe and Frankland by acting upon cyanide of ethyl with potassium; they regarded it at the time as the radical methyl $C_2\,H_3$.

[†] Four volumes, if the volume of the atom of the organic compound in the gaseous state is compared with the volume of one atom of oxygen. (See par. 170.)

radicals are different from all other known hydrocarbons.

202. 2nd.—The boiling-points of these so-called radicals are in favour of their formulæ being doubled.

The student must read the chapter on boiling-points, in order to appreciate their value in the determination of formulæ. We will here briefly state that part which is necessary to this argument. Kopp had observed, that the difference in the boiling temperatures of two analogous substances, differing by $C_2 H_2$, was about 19° C.; the numbers observed were sometimes lower than 19° C., but frequently also they were higher. Now the boiling-points of the three alcohol radicals, valyl, amyl, and caproyl, were found to be as follows (the formula given is the one-volume formula) :—

Name.	Formula.	Boiling-point.	Difference.
Valyl -	- $C_8 H_9$ -	- 108°C.	47
Amyl -	- $C_{10} H_{11}$ -	- 155	
Caproyl	- $C_{12} H_{13}$ -	- 202	47

The anomalous differences exhibited by the boiling points in question, amounting actually, in these instances, for a difference of $C_2 H_2$ to nearly double the maximum ever observed, disappear at once if we adopt formulæ representing two volumes of vapour, as is shown in the following statement, in which the boiling-points of the missing terms* are assumed to be half-way between those of their neighbours :—

Name.	Formula.	Boiling-point.	Difference.
Valyl -	- $C_{16} H_{18}$ -	- 108°C.	23
	$C_{18} H_{20}$ -	- 131·5	23
Amyl -	- $C_{20} H_{22}$ -	- 155	
	$C_{22} H_{24}$ -	- 178·5	23
Caproyl	- $C_{24} H_{26}$ -	- 202	23

203. 3rd.—Hofmann considered that the formulæ of these bodies required to be doubled in order to remove the

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* Since that time one of the missing terms has been discovered, and its boiling-point is given in the table, page 122.

discrepancy exhibited by the boiling-points of hydride of amyl, amyl, and amyline.

Name.	Formula.		Boiling-point.
Hydride of Amyl	$C_{10}H_{11}, H$	(Two volumes)	30°C.
Amyl - -	$C_{10}H_{11}$	(One volume)	155
Amyline - -	$C_{10}H_{10}$	(Two volumes)	39

In commenting upon this discrepancy, Hofmann said, "It appears strange, at the first glance, that the boiling-point of $C_{10}H_{10}$, should be raised more than 100° by the assimilation of one equivalent of hydrogen, whilst we usually find that the addition of hydrogen depresses the boiling-point. And again, that in amyl the boiling-point should be depressed, even in a more striking manner, by its combining with the same amount of hydrogen. But I do not attach," he said, "great importance to this point, inasmuch as the formulæ of these bodies, corresponding to different volumes, cannot well be compared with each other. Moreover, it is but right to state, that we are not very well acquainted with the influence of hydrogen on boiling-points; thus the boiling-point of bromine is considerably higher than that of hydrobromic acid; whilst, on the other hand, hydrocyanic acid boils at a higher temperature than cyanogen itself."

204. 4th.—Hofmann considered that, as these isolated bodies did not combine with the metalloids, and reproduce a methyl, ethyl, or amyl compound, they did not display the character of radicals. Nobody expected, he said, that ethyl, like zinc, would disengage hydrogen from sulphuric acid and water; or that, like iron, it would precipitate copper or antimony. There were, however, many who thought, whether rightly or wrongly, that these substances would, under certain circumstances, like hydrogen, combine directly with chlorine; that they would combine with other elements, without giving rise to the phenomena of substitution, and reproduce, like other of the isolated radicals, as cyanogen, or cacodyl, some terms of their own series. The great difficulty with which free hydrogen combines with chlorine, and the powerful affinity exhibited by the latter element for hydrogen, when in the combined state, militates, it is true, to a certain extent, against this assumption; but we have, on the other hand, in olefiant gas and its congeners, well-known instances in which this

direct combination actually appears to take place. Up to this present moment, none of the supposed alcohol radicals have been observed to combine, like cyanogen, or cacodyl, directly with any of the elements. None of them have been found capable of reproducing a methyl, ethyl, and amyl compound.

205. To this objection, Dr. Frankland thus replied:*—This objection follows naturally from the circumstance that, up to the time of the isolation of these bodies, we were only acquainted with one basic or electro-positive radical in a separate form, viz., cacodyl, which has, unfortunately, been looked upon by some chemists as a type of all other organic radicals, which they therefore expected to find endowed with similar powerful affinities. Such a partial view of the essential characters of a compound radical could not have been formed from a careful comparison of the varied properties of the simple radicals, which are undoubtedly the true types of their representatives in the organic world. A slight glance at the habits and affinities of these elementary bodies exhibit to us the most widely different powers of combination. Commencing with potassium, and terminating with hydrogen, gold, platinum, iridium, and nitrogen, we have a series of bodies which, although they all readily pass from one form of combination to another when already combined, yet when once isolated, exhibit, as we ascend the scale, an increasing reluctance to enter into union.

Taking these reactions of the simple radicals then into consideration, it would be neither difficult nor visionary to predict that their organic representatives would be found possessed of as great a variety of disposition, and that we should have a corresponding series of bodies, commencing with cacodyl, zinc-methyl, zinc-ethyl, stib-ethyl, &c., and terminating with the radicals of the alcohol family (the perfect representatives of hydrogen), exhibiting a similar decrease of combining power; and, since the organic groups are so instable in their nature, and so liable to metamorphosis from the slightest causes, that we are unable to expose them, without utter destruction, to the powerful influences which we can bring to bear upon an elementary body, it surely ought to be a matter of no great surprise if the members of the least electro-positive extremity of the series should elude all our attempts to bring them again uninjured into combination. If nitrogen were decomposed at a red heat, by what means could we recombine that radical when once isolated? I am at present engaged in filling up the gap in the series between cacodyl and ethyl, and have been lately occupied in studying the properties of an organo-metallic radical, which seems to occupy a position about midway in the series, entering into direct combination with several of the metalloids, but with a degree of affinity immeasurably less than that exhibited by cacodyl or zinc-methyl.

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* We have not thought it necessary to give Frankland's replies to Hofmann's other objections, but we strongly recommend the student to study the papers himself. They are full of instruction in every point of view, showing what different views may be taken in organic chemistry, and with what powerful arguments they may be supported:—Hofmann "On the Action of Heat upon Valeric Acid, with some Remarks on the Formulæ of the Alcohol Radicals:" *Journal of the Chemical Society of London*, vol. iii.; and in the same volume of that Journal, "Researches on the Organic Radicals," by Dr. Frankland.

206. Although Hofmann thought the formulæ ought to be doubled for the above reasons, yet he considered the mode of the formation of ethyl and the other alcohol radicals was in favour of the lower formula; for if hydriodic acid and zinc yielded iodide of zinc and hydrogen thus,—

$$H\,I + Zn = H + Zn\,I,$$

iodide of ethyl and zinc ought to give rise to $C_4\,H_5$, and not $C_8\,H_{10}$, thus,—

$$C_4\,H_5\,I + Zn = C_4\,H_5 + Zn\,I.$$

207. Brodie admitted the perfect analogy of the reactions between hydriodic acid and zinc and iodide of ethyl and zinc; but as he regarded the formation of hydrogen by the action of zinc and hydriodic acid to be represented thus,—

$$2\,H\,I + Zn\,Zn = H\,H + 2\,Zn\,I;$$

so he considered the formation of ethyl by the action of zinc on iodide of ethyl to be this,—

$$2\,C_4\,H_5\,I + Zn\,Zn = C_4\,H_5, C_4\,H_5 + 2\,Zn\,I.$$

He therefore considered that the two atoms of ethyl were united together, forming a compound which he called ethide of ethyl,[*] and he proved the truth of this by a series of very ingenious and beautiful experiments. Frankland had shown, as we have already noticed, that when zinc acts on iodide of ethyl in the presence of water, the reaction was thus expressed:—

$$C_4 H_5 I + H O + 2 Zn = \underbrace{C_4 H_5, H}_{\text{hydride of ethyl.}} + Zn I, Zn O.$$

This, Brodie said, may be taken as the type of the other changes; for substituting, in the change, iodide of ethyl for water, we have the formation of ethide of ethyl:—

$$2 C_4 H_5 I + Zn\, Zn = \underbrace{C_4 H_5, C_4 H_5}_{\text{ethide of ethyl.}} + 2 Zn I;$$

or, substituting water for the iodide of ethyl, we have the formation of hydrogen, thus:—

$$2 H O + Zn\, Zn = H\, H + 2 Zn O,$$

a reaction which truly takes place at high temperatures.

208. Brodie traced out by experiment that the first action of zinc on iodide of ethyl does not consist in the liberation of ethyl, thus,—

$$C_4 H_5 I + Zn = C_4 H_5 + Zn I;$$

but in the formation of zinc ethyl, thus,—

$$C_4 H_5 I + Zn\, Zn = C_4 H_5, Zn + Zn I.$$

That this zinc ethyl then reacts upon a fresh portion of iodide of ethyl, thus,—

$$C_4 H_5, Zn + C_4 H_5 I = C_4 H_5, C_4 H_5 + Zn I.$$

209. The formation, therefore, of hydrogen from the action of zinc on hydrochloric or hydriodic acid, must consist of two stages, although we have not yet been able to prove it experimentally; because, under the circum-

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[*] The doubling of the formulæ of the alcohol radicals, proposed by Hoffmann, Laurent, and Gerhardt, and Brodie's views of the constitution of the radicals, are totally different. By doubling the formulæ they would have had the general formula (Cn Hn + 2), and have been made members of the class of hydro-carbons called the Marsh-gas group; according to Brodie, they are isomeric with the members of the marsh-gas group, but not identical with them.

stances under which it is generally formed, the hydride of zinc is decomposed as fast as it is created.

1st Stage.—$HI + ZnZn = ZnH + ZnI$.
2nd Stage.—$ZnH + HI = HH + ZnI$.

210. The student must, however, observe, that the formation of molecular atoms of the alcohol radicals was not proved by the simultaneous liberation of two atoms of ethyl by the action of iodide of ethyl on zinc-ethyl, and the analysis of the substance could not aid in the proof. But Brodie at once suggested a mode of proving the existence of these molecular atoms by analogy. He said the next step in these experiments should be the decomposition of iodide of methyl (C_2H_3I), or iodide of amyl ($C_{10}H_{11}I$), by zinc-ethyl; in which case, he said, the formation of a compound hydro-carbon might be anticipated of the formula C_2H_3, C_4H_5 (ethyl-methyl), or $C_{10}H_{11}, C_4H_5$ (ethyl-amyl).* Since that time Wurtz has actually obtained a series of these double radicals by decomposing, by means of sodium, equivalent proportions of the iodides. Thus, in the preparation of ethyl-amyl the following reaction occurs:—

$$C_4H_5I + C_{10}H_{11}I + NaNa = C_{10}H_{11}, C_4H_5 + 2NaI.$$

211. The formation of these heterogeneous radicals affords very strong analogical proof of the existence of *molecular atoms* of the homogeneous radicals. This is confirmed by the boiling-points and vapour-densities of these bodies. The boiling.point of the heterogeneous radicals rises gradually as the number of equivalents of carbon and hydrogen increases; and this regular progression takes place in the homogeneous radicals if they are represented by the double atom; the vapour-densities as well as the boiling-points of the homogeneous radicals are what would be theoretically assigned to them, if we represented them by the double atom. These proofs show that the homogeneous and heterogeneous radicals are both constructed upon the same molecular plan, and that Brodie's view of their constitution is the correct one.

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* We refer the student to the original memoir by Brodie, "Observations on the Constitution of the Alcohol Radicals, and on the Formation of Ethyl," in the *Journal of the London Chemical Society*, vol. iii.

Names.	Formulæ.	Specific Gravity.			Boiling-point.	Difference.
		Liquid.	Expt.	Theory.		
Ethyl*-tetryl†	$C_{12}H_{14}=C_4H_5, C_8H_9$	0·7011	3·053	2·972	62	26
Ethyl-amyl	$C_{14}H_{16}=C_4H_5, C_{10}H_{11}$	0·7069	3·522	3·455	88	
Methyl*-hexyl‡ ...	$C_{14}H_{16}=C_2H_3, C_{12}H_{13}$	...	3·426	3·455	82	18
Tetryl (Tetrylide of tetryl) ...	$C_{16}H_{18}=C_8H_9, C_8H_9$	0·7057	4·070	3·939	106	26
Tetryl-amyl	$C_{18}H_{20}=C_8H_9, C_{10}H_{11}$	0·7247	4·465	4·423	132	26
Amyl (Amylide of amyl)	$C_{20}H_{22}=C_{10}H_{11}, C_{10}H_{11}$	0·7413	4·899	4·907	158	
Tetryl-hexyl	$C_{20}H_{22}=C_8H_9, C_{12}H_{13}$	...	4·917	4·907	155	44
Hexyl (Hexylide of hexyl)	$C_{24}H_{26}=C_{12}H_{13}, C_{12}H_{13}$	0·7574	5·983	5·874	202	

212. "It may further be remarked, in illustration of the pre-existence of the original molecular arrangement of the component groups of these compound bodies, that Wurtz finds that amyl preserves its rotatory action on a ray of polarized light when it passes into these compounds, ethyl-amyl displaying the power of rotating a polarized ray to the right; whilst amyline, valeric acid, and other derivatives of amylic-alcohol, in which there is reason to suppose that the molecule of amyl is destroyed, exert no rotatory power."

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* Methylide of methyl and ethylide of ethyl are both gases at the ordinary temperature, they are not liquefied by a cold of 0° F.

† *Tetryl*, *butryl* or *valyl*.

‡ *Hexyl* or *caproyl*.

CHAPTER IV.

NUMERICAL RELATIONS OF EQUIVALENT NUMBERS.—BINARY THEORY OF SALTS.

Numerical relations of equivalent numbers, 213. *The views of Prout, Thomson, and Dumas, on the atomic weights of bodies*, 213. *The views of Berzelius and Stas on the atomic weights of bodies*, 218. *Binary theory of salts*, 219. *Facts which appear to support the binary view*, 221. *Both views of the constitution of salts hypothetical*, 227. *Objections to the binary theory*, 227. *Exercises*, 229.

213. *Numerical relation of equivalent numbers.*—As the atomic weights of carbon, oxygen, sulphur, bromine, and many of the other elements, are *exact* multiples of that of hydrogen, Prout and Thomson considered that it was a law of nature that the atomic weights of all the other elements are divisible by that of hydrogen. If this were the case, it might be supposed that hydrogen was the only elementary body, and that the larger and heavier atoms of the other so-called elementary bodies are produced by a combination of the requisite number of atoms of hydrogen, and that these different combinations of the hydrogen atoms are the cause of the difference in properties exhibited by the different bodies. Dumas has devoted great attention to this subject, and he concludes, from the results of his investigations, that, in a modified sense, Prout's law is true; and he considers that the elementary bodies, the atomic weights of which he regards as accurately known, may be arranged in three groups, viz.:—

1. Bodies which are represented by multiples of a whole number of hydrogen.
2. Multiples by the number 0·5 of that of hydrogen.
3. Multiples by 0·25 of that of hydrogen.

1. Bodies which are multiples by a whole number of the equivalent of hydrogen:—

Hydrogen	1	Molybdenum	48
Carbon	6	Cadmium	56
Oxygen	8	Tin	59
Nitrogen	14	Arsenic	75
Silicon	14	Bromine	80
Sulphur	16	Tungsten	92
Fluorine	19	Mercury	100
Calcium	20	Silver	108
Sodium	23	Antimony	122
Iron	28	Iodine	127
Phosphorus	31	Bismuth	210

2. Multiples by 0·5 of the equivalent of hydrogen:—

Manganese	27·5	Tellurium	64·5
Cobalt	29·5	Barium	68·5
Nickel	29·5	Osmium	99·5
Chlorine	35·8	Lead	103·5

3. Multiples by 0·25 of the equivalent of hydrogen:—

Aluminum	13·75	Selenium	39·75
Copper	31·75	Strontium	43·75
Zinc	32·75		

214. The relations exhibited between the members of many of these bodies which are chemically allied, are often very remarkable.

1. Thus it has been observed that, in several instances where two elements are in close chemical relation to each other, they have atomic weights which are identical, and in others they are nearly identical, as in the following examples:—

Cobalt and nickel	29·5
Lanthanum and cerium	40·0
Rhodium and ruthenium	52·1
Platinum and iridium	98·5

215. The following have nearly equal atomic weights:—Chromium, 26·7; manganese, 27·5; iron, 28. Copper, 31·75, and zinc, 32·75. Platinum, 98·7; iridium, 98·7; and osmium, 99·6.

2. In other cases, the ratio of the atomic weights is as 1 to 2; for instance:—

Oxygen = 8 | Sulphur = 16
Aluminum = 13·75 | Manganese = 27·5

3. We are enabled to arrange the various substances reputed elementary, by certain resemblances, into various well-marked groups; and those composing the same group are capable of substituting one another in compounds, without altering the general character of the body. Such a group is the triad—chlorine, bromine, iodine. Now, all the essential qualities of bromine are intermediate between those of chlorine and iodine, and so is its atomic weight. Thus, could we by any means take half an atom of chlorine, and add to it half an atom of iodine, we might expect to produce bromine. Similar triads are found in sulphur, selenium, and tellurium; lithium, sodium, and potassium; and calcium, strontium, and barium. It is a curious and interesting fact that several members of any one of these triads are generally found together.

216. Despretz has attempted to ascertain whether certain of the so-called elements are decomposable; and he concluded from his researches that they are incapable of decomposition. Dumas, in reply to Despretz, prefaced his remarks by presenting the following table, which exhibits an interesting relation between the equivalents of certain simple and compound bodies:—

Fl 19, Cl 35·5, Br 80, I 127 }
N 14, P 31, As 75, Sb 122 } Difference, 5.

Mg 12·25, Ca 20, Sr 43·75, Ba 68·5, Pb 103·5 }
O 8, S 16, Se 39·75, Te 64·5, Os 99·5 } Diff. 4.

Ammonium 18, Methylamine 32, Ethylamine 46,
Propylamine, 60, &c. - - - - - - }
Methylium 15, Ethylium 29, Propylium 43, Butylium, 57, &c. - - - - - - } Diff. 3.

217. Since the radicals (elements) in mineral chemistry present the same general relations as those in organic, Dumas believes there is reason for bringing the two branches more closely together than is usually done. We can decompose the latter, and there is no proof that we may not decompose the former. He thus sums up his conclusions:—(1.) The compounds which the three king-

doms offer for our study, are reduced by analysis to a certain number of radicals, which may be grouped in natural families. (2.) The characters of these families show incontestable analogies. (3.) But the radicals of mineral chemistry differ from the others in this,—that if they are compounds, they have a degree of stability so great that no known forces are capable of producing their decomposition. (4.) The analogy authorises the inquiry whether the former may not be compound, as well as the latter. (5.) It is necessary to add, that the analogy gives us no light as to the means of causing this decomposition; and if ever to be realized, it will be by methods or forces yet unsuspected.

218. As the atomic weights of most bodies are not multiples by whole numbers of that of hydrogen, Berzelius regarded the occasional near divisibility of these weights by that of hydrogen, as merely accidental. And Stas, who has recently published a long and most laborious series of researches upon the atomic weights of the elements, considers that the law of Prout is a pure illusion, and he thinks we should regard the indecomposable substances of our globe as distinct bodies, having no simple relations between their atomic weights; and that the undeniable analogy in properties, which is observed in certain of the elements, must be sought for in other causes than those derivable from the relations in weight of their acting masses.

219. *Binary theory of salts.*—In a former work* we gave the view of the constitution of salts which is most generally received. According to this view, salts are subdivided into two classes; to the one class belong all salts made up of an oxygen acid and an oxygen base; they are therefore called *oxygen salts.* To the other class belong all salts formed by the union of the radicals in hydrogen acids with some metal. These binary salts are called *haloid salts* (from αλς, sea-salt, and ειδος, form), because they are constructed upon the same plan, or type, as sea-salt. As the two classes of salts resemble each other in properties, Davy considered they might be constructed upon the same plan or type, and that instead of regarding oxygen salts as composed of an oxide of a

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* The "First Step in Chemistry."

metal and the anhydride of an hydrated oxygen acid, they might be regarded as composed of a metal and a compound salt radical, having the same chemical relations as the radicals in the hydrogen acids. According to this view, sulphuric acid and the sulphates are thus represented:—H. $S O_4$, M. $S O_4$: and nitric acid and the nitrates thus:—H. $N O_6$, M. $N O_6$. The salt radical, $S O_4$, is called sulphion. The compounds formed by a combination of it with the metals or hydrogen, are called sulphionides. H. $S O_4$, is called sulphionide of hydrogen; Na, $S O_4$ is called sulphionide of sodium, &c. In the same way, $N O_6$ is called nitration; its compounds with the metals and hydrogen are called nitrationides; $H N O_6$ is called nitrationide of hydrogen, and $Na N O_6$ is called nitrationide of sodium, &c. "The class of oxygen acid salts is thus abolished, and they become binary compounds, like the chlorides and cyanides. Even oxygen acids themselves can no longer be recognised. It is not sulphuric acid ($S O_3$), but what was formerly viewed as its compound with water, that is the acid, and it is a hydrogen acid.

220. "On this view, it is obvious that the acid and salt are really bodies of the same constitution; hydrochloric acid being the chloride of hydrogen, as common salt is the chloride of sodium, and sulphuric acid, and sulphate of soda, being the sulphionides of hydrogen and of sodium. The acid reaction and sour taste are not peculiar to the hydrogen compound, and do not separate it from the others; the chloride, sulphionide, and nitrationide of copper being nearly as acid and corrosive as the chloride, sulphionide, and nitrationide of hydrogen, and clearly bodies of the same character and composition;—they are all equally salts in constitution. The term 'acid' is not absolutely required for any class of bodies included in the theory, and might, therefore, be dropped, if it were not that an inconvenience would be felt in having no common name for such bodies as anhydrous sulphuric acid, $S O_3$; anhydrous nitric acid, $N O_5$; sulphurous acid, $S O_2$; carbonic acid, $C O_2$, &c. To these substances, which first bore the name, it should now be confined. In considering the generation of salts, three orders of bodies would be admitted, as in the following tabular exposition of a few examples:—

I. The acid.	II. The salt radical.	III. The salt.
SO_3	SO_4	$SO_4 + H$ or a metal.
NO_5	NO_6	$NO_6 + H$,,
	NC_2	$NC_2 + H$,,
	Cl	$Cl + H$,,

"The first term of the series, or 'the acid,' is wanting in the last two examples, and that is the peculiarity of those bodies which constituted the original class of hydrogen acids and their salts; while to the old class of oxygen acid salts, both an acid and a salt radical can be assigned, as in the first two examples."—*Graham.*

221. According to the salt-radical theory, the three modifications of phosphoric acid are explained by supposing that each modification contains a different salt radical. Thus:—

	Ordinary view.	Binary view.
Monobasic phosphoric acid	HO, PO_5	H, PO_6
Bibasic ,, ,,	$2HO, PO_5$	H_2, PO_7
Tribasic ,, ,,	$3HO, PO_5$	H_3, PO_8

By the *old view*, the acid PO_5, can combine with water in three different proportions. This is also the case with the acid SO_3, as we know three distinct hydrates of sulphuric acid, viz., HO, SO_3; $2HO, SO_3$; and $3HO, SO_3$. Each of these hydrates of sulphuric acid is neutralized by one equivalent of base, and therefore the same salt, composed of one equivalent of base, and one of acid, is produced in each case. But this is not the case with phosphoric acid; its capacity of saturation depends upon its state of hydration, and therefore the three hydrates give rise to three different classes of salts. HO, PO_5 requires but one equivalent of base to form a neutral salt, while the acid $2HO, PO_5$ requires two equivalents, and the acid $3HO, PO_5$, requires three equivalents of base to form neutral salts. Upon the old view of the constitution of acids and salts, no satisfactory reason can be assigned for the cause of this difference; but the *binary* view gives one which appears to be perfectly satisfactory. According to this view, the three so-called hydrates differ from each other by containing a different salt radical, united with a different quantity of hydrogen and as neutral salts are formed from hydrogen acids, by the substitution of a metal for the hydrogen they contain, the different modifications of phosphoric acid, owing to their containing different atomic proportions of replaceable hydrogen, require different proportions of base to neutralize them, and accordingly they give rise to different classes of salts. Sulphuric acid, although it combines, according to the old view, with water in three different proportions, giving rise to three different hydrates, forms only one class of salts, because the three hydrates contain the same quantity of hydrogen, replaceable by a metal, as will be seen when the formulæ are written according to the binary view, thus,—$H\,SO_4$; $H\,SO_4, HO$; $H\,SO_4, 2HO$.

222. The binary view of the constitution of the phosphates appears to receive support from the changes which the three classes of salts undergo when subjected to electro-chemical decomposition. The salts are decomposed; the *acids travel unaltered.* A tribasic salt giving, at the positive electrode, a solution of the tribasic acid; a bibasic salt, a solution of the bibasic acid; and a monobasic salt, a solution of the monobasic acid. The conversion, by ignition, of ordinary phosphate of soda ($2\,NaO, HO, PO_5 + 24$ aq.) into bibasic phosphate of soda, and acid phosphate of soda ($NaO, 2\,HO, PO_5$) into monobasic phosphate of soda, can be satisfactorily explained on the binary view. Example:—When ordinary phosphate of soda is exposed to a temperature of 300° F., the 24 atoms of water of crystallization are expelled; the dried salt, when dissolved in water, gives all the chemical reactions of the original salt; and if the solution be evaporated to dryness, the phosphate of soda is obtained in its original crystalline form; but if the dry residue be heated to redness, an additional atom of water escapes, and on dissolving the residue in water, the phosphate is found to be transformed into a phosphate belonging to another class. The explanation of the change, according to the binary theory, is this:—The formula of phosphate of soda is $2\,NaH, PO_8 + 24$ aq.; it can lose the 24 atoms of water without altering its constitution; but when the hydrogen is expelled, it removes, on its expulsion, one atom of oxygen from the salt-radical, and converts it, by this removal, into another salt-radical,

$P\,O_7$, which is bibasic. In like manner, if acid phosphate of soda, $Na\,H_2\,P\,O_8$, be heated to redness, the two atoms of hydrogen are expelled, and they remove two atoms of oxygen from the salt-radical, and convert it, by this removal, into another salt-radical, $P\,O_6$, which is monobasic.

223. "One remarkable consequence deducible from the theory under consideration is, that those oxides which most easily lose oxygen, should most readily replace by their metal the hydrogen of the acid. This is found to be the case. For example—potash can only replace by potassium two of the three equivalents of hydrogen in cyanuric acid, and one of the two equivalents of hydrogen in fulminic acid, forming the compounds—$Cy_3\,O_6\left.\begin{matrix}K_2\\H\end{matrix}\right\}$ and $Cy_2\,O_4\left.\begin{matrix}K\\H\end{matrix}\right\}$, while, with oxide of silver, an easily reducible oxide, the replacement, as before mentioned, is complete. This fact furnishes an almost irresistible argument for the existence of hydrogen, as such, in acids; and further explains the formerly unaccountable fact, that the neutral salts formed by the action of oxide of silver on organic acids, are always anhydrous." If, in acids, the hydrogen existed combined with oxygen, as water, it ought to be expelled most readily by the strongest bases; whereas the reverse is the fact, as shown by the above examples.

224. The liberation of hydrogen, on the addition of sulphuric acid to zinc, can be explained in a simple and philosophical manner by the binary theory; the hydrogen is simply displaced in its combination with sulphion by the zinc; whereas, upon the old hypothesis, the explanation is most unsatisfactory. The zinc, according to this view, *does* and *does not decompose* water. It decomposes water when that compound is combined with an oxygen acid, but it does not decompose the water when that compound is free.

225. The phenomena which attend the decomposition of the oxysalts in the voltaic circle, admit of the most satisfactory explanation on the binary theory. It is a fundamental law of voltaic action, that the amount of force circulating in any circuit at the same time, is equal in every vertical section of the circuit, and, consequently, its decomposing energy in each section must also be

equal; and an atom of any electrolyte requires for its decomposition the same *quantity* of electricity as an atom of any other. Thus the *quantity* of electricity which will decompose one atom of water, will decompose one atom of chloride of lead, one of oxide of silver, or one atom of any electrolyte. Now, on decomposing an oxysalt of the alkalies or alkaline earths,—say sulphate of soda,—for every atom of water, or chloride of lead, which is decomposed in the voltameter placed in the course of the circuit, one atom of $S\,O_3$, and one atom of oxygen, accumulates at one electrode (the zincode), whilst one atom of soda, and one of hydrogen, is set free at the other electrode (the platinode); yet we have stated that it is a fundamental law of voltaic action, that the amount of force circulating in any circuit at the same time, is equal in every vertical section of the circuit; and, consequently, its decomposing energy in each section must also be equal. Also that an atom of any electrolyte requires for its decomposition the same quantity of electricity as an atom of any other; yet for every atom of the electrolyte decomposed in the voltameter, we have one equivalent of sulphate of soda, and one equivalent of water, decomposed. Now, on the binary theory, sulphate of soda is not composed of soda and $S\,O_3$, but sodium and sulphion ($S\,O_4$); the sodium, therefore, is liberated at the platinode, whilst sulphion is liberated at the zincode. But the sodium cannot exist in a free state in the presence of water, and sulphion cannot exist free; both the simple and compound radical, therefore, decompose water as soon as they are liberated; the sodium combines with the oxygen, setting the hydrogen free, whilst the sulphion combines with hydrogen, setting the oxygen free: therefore, hydrogen is liberated along with soda at the platinode, and oxygen is liberated along with sulphionide of hydrogen at the zincode; and in equivalent proportions, because an atom of water is decomposed by every liberated atom of sodium, and an atom of water by every liberated atom of sulphion. According to this explanation, only one atom of one electrolyte sulphionide of sodium is decomposed, for each atom of the electrolyte which is decomposed in the voltameter, as the decomposition of the water is occasioned, as we have seen, by a secondary action. If the *metal* of the salt is one which does not decompose water at ordinary temperatures, then no hydrogen, but only the metal in its uncombined state, is set free at the platinode, whilst sulphionide of hydrogen and oxygen are found at the zincode, owing to the sulphion decomposing water.*

226. Kopp considered that the binary theory of salts was supported by the atomic volume of salts, but Filhol has shown that the experimental results may be explained quite as well by the older view of the constitution of salts; we shall, therefore, defer noticing Kopp's views until we come to consider the atomic volume of solids.

227. Both views of the constitution of salts are hypothetical, and although many chemical changes can be explained, as we have seen, in a more simple and philosophical manner by the binary view than by the old one, yet there are many objections to the binary theory, and it will, probably, give place to other and still newer views of the constitution of salts, which we shall presently bring before the attention of the student. Our objection to the salt-radical theory is the necessity of creating a great number of compound radicals, which never have and probably never will be isolated, such as $S\,O_4$, $N\,O_6$, $C\,O_3$, &c. Another objection Professor Miller thus states:—"It appears to be highly improbable that a body of such powerful affinities as potash should, in carbonate of potash for example, part with its oxygen to a substance which, like carbonic acid, exhibits no tendency to further oxidation, so that $K\,O,\ C\,O_2$, should become $K,\ C\,O_3$."

228. Hess observes on Daniell's theory,—"The theory which regards sulphate of soda as $Na\,S\,O_4$, certainly affords the simplest explanation of its electrolysis. Since, however, many weighty reasons may be urged against the adoption of this hypothesis, the following explanation may for the present be admitted. Sulphate of soda is $Na\,O,\ S\,O_3$; decomposition by the electric current is exerted only on the soda (since, by Faraday's law,† $S\,O_3$ is incapable of direct decomposition). Sodium separates at the negative pole, where it decomposes water and

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* The student who desires to pursue the subject further is referred to the second part of Miller's "Elements of Chemistry," or to the original memoirs on this subject by Drs. Daniell and Miller, in the "Phil. Trans." 1844.

† See the Author's "First Step in Chemistry," 3rd edition, p. 177.

yields soda and hydrogen gas. The oxygen which was combined with the sodium is transferred, together with the sulphuric acid, to the adjacent atom of sodium. An atom of oxygen is set free at the positive pole; and since the sodium which was combined with it goes towards the negative pole, the sulphuric acid is set free by secondary action, or rather it passes from its state of combination with soda into that of combination with water. In the case of sulphate of copper, &c., similar actions take place, excepting that the metal liberated by the current does not decompose water.

229. The formulæ of the following salts must now be written out in accordance with the binary theory.

EXERCISES.

110. Bisulphate of soda.
111. Sulphate of alumina.
112. Nitrate of ammonia.
113. Chlorate of potash.
114. Bromate of soda.
115. Sulphate of potash and magnesia.
116. Phosphate of silver (monobasic phosphate).
117. Phosphate of alumina ,, ,,
118. Phosphate of silver (bibasic phosphate).
119. Phosphate of alumina ,, ,,
120. Phosphate of silver (tribasic phosphate).
121. Phosphate of alumina ,, ,,

CHAPTER V.

POLYMORPHISM, PSEUDOMORPHISM, ISOMORPHISM.

Dimorphism, 230. *Trimorphism*, 231. *Influence of heat in causing bodies to crystallize in one system or another*, 233. *The different crystalline forms of the same substance not of equal stability*, 234. *Examples. Isodimorphism*, 235. *Examples. The same substance in its different crystalline forms differs in its physical characters*, 236. *Examples. List of dimorphous bodies*, 237. *Pseudomorphism*, 238. *The processes by which pseudomorphs are produced*, 240. *Isomorphism*, 243. *Behaviour of two or more non-isomorphous crystalline substances in the same solution during crystallization*, 244. *Behaviour of two or more isomorphous crystalline substances in solution during crystallization*, 246. *Intermixture of isomorphous substances in minerals*, 249. *Table of some of the most important groups of isomorphous substances*, 251. *Graham's opinion upon the isomorphous relations of water*, 252. *Scheerer's view upon the isomorphous relations of water*, 253. *Polymeric isomorphism*, 254. *The method for deducing the rational formula for compounds containing isomorphous constituents*, 255. *System of notation employed in mineralogical works*, 259. *Exercises. The different reasons which have been suggested in explanation of the phenomena of isomorphism*, 261. *Kopp's view that isomorphous bodies have the same equivalent volume*, 263. *Some of the views held upon bodies with like forms but unlike constitutions*, 265. *The chief points which have been brought before the notice of the student*, 266. *Aid derived from isomorphism in determining equivalents*, 268.

230. POLYMORPHISM.—Some elementary and compound bodies are capable of assuming two distinct crystalline forms; substances which can thus crystallize, according to two different systems,* are called *dimorphous* (from

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* The names and definitions of the six systems into which crystals are subdivided, are given at p. 142.

δὶς, twice, and μορφή, shape), and the phenomenon itself has received the name of dimorphism. Example.—The crystals of carbonate of lime in calcareous spar and in arragonite belong to different systems of crystallization.

231. Some substances are even *trimorphous*, that is, they crystallize in three different systems. Both the seleniate of zinc (Zn O, Se O_3 + 7 aq.), and sulphate of zinc (Zn O, S O_3 + 7 aq.), and the seleniate of nickel (Ni O, Se O_3 + 7 aq.), and sulphate of nickel (Ni O, S O_3 + 7 aq.), according to Mitscherlich, exhibit this peculiarity.

232. Laurent and Pasteur have observed that the forms of dimorphous crystals border upon the limits of the two systems, and under the influence of certain determining conditions, can pass easily out of the one into the other system.

233. Whether a body shall crystallize in one system or another seems to depend chiefly on temperature. Examples.—Carbonate of lime artificially prepared takes the form of calc-spar or arragonite, according as it is precipitated at the temperature of the air or near the boiling point of water. Sulphur, in crystallizing from solution in bisulphide of carbon or in oil of turpentine, at a temperature under 100° F., forms octohedrons with rhombic bases, but when melted by itself and allowed to cool slowly, it assumes the form of an oblique rhombic prism on solidifying at 232° F. Crystals formed at one particular temperature, and then exposed to that temperature at which the substance assumes its other crystalline form, frequently become changed, without alteration of external form, into an aggregate of small crystals of the latter kind; the change from one form to the other is often attended with a change in the crystals from transparency to opaqueness. Example.—We have already noticed that sulphate of nickel crystallizes in three forms; "it crystallizes below 59° F. in right rhombic prisms; between 59° and 68° in acute square-based octohedrons; and when the temperature is above 86° in oblique rhombic prisms. In the first case, the crystals belong to the prismatic; in the second to the pyramidal, and in the third to the oblique system. If the right rhombic crystals be placed in the summer's sun for a few days they become *opaque*, but still retain the

form of the *prism*, which is found, when broken, to consist of a mass of *octohedrons*."

234. The two or three forms are not, however, of equal stability. "*One* of the forms appears to be the stable condition of arrangement; the other forms appear to be produced by the sudden fixation of the molecules, in a form which is naturally only transitive, and from which they free themselves as soon as the external circumstances admit of their suitable motion amongst each other." A *change of temperature* is sufficient to produce this alteration in form. In some cases it can be brought about by *mere rubbing;* and in others it appears to be produced *without the aid of any external agent.**

EXAMPLES.

1. When a prism of arragonite is heated in the flame of a spirit-lamp, it breaks up into a congeries of little rhombs of common calc-spar, at a temperature far below that at which the carbonate lime commences to be decomposed; but no alteration of temperature can convert calc-spar back again into arragonite. Indeed, arragonite appears to be formed only between very narrow limits of temperature. We have noticed (233) that at 212° F., artificially prepared carbonate lime takes this form, but below that point it takes the form of calc-spar; and we now see that at temperatures higher than 212° F., arragonite becomes converted into calc-spar.

2. Proto-iodide of mercury separates from solution, and likewise sublimes at a very gentle heat, in scarlet tables, belonging to the square prismatic system; but when

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* In solid bodies, a difference of molecular structure, fully equivalent to that to which dimorphism may be referred, is capable of being produced by very simple means. Thus, when a plate of glass is compressed by means of a screw, it assumes a doubly refracting structure, and gives, with polarized light, a cross, and rings, variously disposed, according to the direction of the pressure. In this case, the change of structure arises, necessarily, from an increase of density in the compressed portions; but the same effect may be produced by the converse process. A plate of glass which has been suddenly cooled from having been red-hot, assumes a similar double refracting and polarizing structure, although here the density is diminished, in place of being increased. I have found the specific gravity of glass, suddenly chilled, to be about $\frac{1}{150}$ less than that of glass of the same kind which had cooled slowly, indicating that the volume was the same that it had occupied at a dull red heat, and that hence the internal molecules were arranged so as to occupy a greater space than in the usual condition.—*Sir R. Kane.*

sublimed at a higher temperature, in sulphur-yellow rhombic tables, of the oblique prismatic system. The red crystals turn yellow as often as they are heated, and resume their red tint on cooling. The yellow crystals obtained by sublimation retain their colour when cooled; but on the slightest rubbing or stirring with a pointed instrument, the part which is touched turns scarlet; and this change of colour extends with a slight motion, as if the mass were alive, throughout the whole group of crystals, as far as they adhere together. In this case, the yellow crystals retain their external form unchanged, while the compound atoms must have taken up the relative position which belongs to the red crystals; the yellow crystals are therefore *pseudomorphous*. The same crystals turn yellow every time they are heated, and red again on cooling. The original red crystals also turn yellow when heated, and retain this colour, after cooling, for several days, even when touched with foreign bodies; and at length spontaneously, but very slowly, resume their red colour. When the red crystals are sublimed at a very gentle heat, red and yellow crystals sublime together. If a glass plate, having both red and yellow crystals on it, be warmed so gently that the red ones do not change colour, but sublimation, nevertheless, goes on, both red and yellow crystals collect on a plate held above the former. Now, since the upper plate is cooler than the lower, and the latter is not hot enough to change the colour of the red crystals, the yellow crystals in the upper plate can have only come from those of the same colour on the lower; they must, therefore, have sublimed as yellow crystals, and the vapour of the yellow crystals must be different from that of the red ones.

3. If melted sulphur be allowed to cool slowly, till a portion of it has become solid, and the still liquid portion be then poured out, the solidified portion exhibits oblique rhombic prisms, belonging to the oblique prismatic system. These are at first perfectly transparent, of a deep yellow colour, and somewhat harder and denser than those of sulphur crystallized in the cold; but after being kept for a few days at the ordinary temperature, they become opaque, of a straw-yellow colour, and become changed into a mass of very minute bright rhombic octohedrons.

4. When arsenious acid is crystallized in rhombic

prisms, it alters slowly, and eventually becomes a dull white mass, which is a congeries of regular octohedrons; but if the rhombic form of the acid be dissolved in muriatic acid, and the solution set to crystallize, it is deposited in the octohedral form, and the formation of each crystal is accompanied by a brilliant flash of light, indicating, probably, the moment of change of molecular condition.

235 When two salts are *iso-dimorphous—i. e.*, they are capable of crystallizing in two different forms, which are similar each to each—we generally find that the stable and more commonly occurring form of one of the salts is not the stable and more commonly occurring form of the other salt.

EXAMPLES.

1. Carbonate of lime, and carbonate of lead, are isodimorphous. The more stable form of carbonate of lime is, as we have seen, calc-spar; the more stable form of carbonate of lead is the same as that of arragonite, the other form of carbonate of lime.

2. Nitrate of potash, and nitrate of soda are isodimorphous; but nitrate of potash usually crystallizes in right rhombic prisms, and nitrate of soda in rhomboids.

3. Arsenious acid, and teroxide of antimony, are isodimorphous; but arsenious acid generally crystallizes in regular octohedrons, and teroxide of antimony in a form belonging to the right prismatic system.

236. The same substance, in its different crystalline forms, differs remarkably in its physical characters; and these differences are perceptible even in the finest particles that can be obtained by mechanical means. The two forms differ in *hardness*, *specific gravity*, and *sometimes in colour*. In one form the substance is *more soluble* than in the other. "A body, in its dimorphous conditions, presents frequently a difference of chemical properties deserving of particular notice. The bisulphide of iron, in its cubical form, is remarkably permanent, not being acted on either by air or water; but in its right rhombic form, when exposed to moist air, it absorbs oxygen with avidity, and is converted into a crystalline mass of copperas. On this principle depends, most probably, the change of molecular condition which takes

place in oxide of chrome, peroxide of tin, zirconia, and alumina, when exposed to a temperature just below redness. These substances, which had been easily soluble in acids, become almost totally insoluble, except in boiling oil of vitriol; and this change is generally accompanied by the spontaneous ignition of the body, which the temperature applied would be quite insufficient to produce."* The student will have noticed that the two forms of iodide of mercury differ in colour. We will now give two examples, the first to show that two forms differ in specific gravity; the second to show that the substance in one form is more soluble than in the other.

EXAMPLES.

1. The specific gravity of carbonate of lime in the form of calc-spar is 2·72; in the form of arragonite it is 3·00; consequently carbonate of lime possesses two different atomic volumes.

2. "Nitrate of potash usually crystallizes in prisms in the form of arragonite; but if a drop of the aqueous solution of this salt be left to evaporate on a glass plate, and the crystallization observed under the microscope, it will be found that side by side with the prismatic crystals, at the edges of the drop, a number of obtuse rhomboids of the calc-spar form are produced, just like those in which nitrate soda crystallizes. As the two kinds of crystals increase in size, and approach one another, the rhomboids become rounded off and dissolve, *because they are more easily soluble than the others*, while the arragonite-shaped prisms go on increasing in size. When the two kinds of crystals come into immediate contact, the rhomboidal ones instantly become turbid, acquire an uneven surface, and after a short time throw out prisms from all parts of their surfaces. Contact with foreign bodies also brings about the transformation of the rhomboids while they are wet. If the drops are so shallow that the liquid dries round the rhomboids before they are disturbed, they will remain for weeks without disintegrating, and bear gentle pressure with foreign bodies without alteration; but stronger pressure, or scratching, or the mere contact of a

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* Sir R. Kane's "Elements of Chemistry," 2nd edition.

prismatic crystal of saltpetre, causes them to change, a delicate film proceeding, as it were, from the point of contact, and spreading itself over their surfaces; they then behave towards foreign bodies like a heap of fine dust, but retain their transparency. The rhombohedrons are also transformed, without alteration of external appearance, when heated considerably above 100° C.; they then become much harder, because the fine powder first produced bakes together into prismatic crystals."

237. The following is a list of dimorphous bodies:—

Sulphur
Carbon
Copper
Dinoxide of Copper
Disulphuret of Copper
Sulphuret of Silver
Sulphuret of Manganese
Oxide of Lead
Bisulphuret of Iron
Iodide of Potassium
Biniodide of Mercury
Bichloride of Mercury
Protoxide of Lead
Arsenious Acid
Oxide of Antimony
Oxide of Titanium
Carbonate of Lime
Carbonate of Magnesia
Carbonate of Iron
Carbonate of Lead
Nitrate of Potash
Nitrate of Soda
Chromate of Lead
Sulphate of Nickel
Seleniate of Zinc
Sulphate of Magnesia
Bisulphate of Potash
Bisulphate of Soda
Sulphate of Magnesia
Garnet
Baryto-Calcite.

238. PSEUDOMORPHISM.—*Pseudomorphous* (from ψεῦδος, a falsehood, μορφη, form) *crystals are those which have the composition of one crystalline substance and the form of another.*

(1.) "Crystals sometimes undergo a change of composition from aqueous agency, or some other cause, without losing their form: for example, octohedrons of spinel change to steatite, still retaining the octohedral form; cubes of pyrites are altered to red or brown iron ore; anhydrite becomes gypsum by the addition of water.

(2.) "*Again:* Crystals are sometimes removed entirely, and at the same time, and with equal progress, another mineral is substituted. For example, cubes of fluor spar may be transformed to quartz, without a change of form. The petrifaction of wood is of the same kind. This process may extend only to the surface of a crystal; and if its interior is subsequently dissolved out, a hollow pseudomorph results.

(3.) "*Again:* Cavities left empty by a decomposed crystal are refilled by another species, by *infiltration*, and the new mineral takes on the external form of the original mineral, as a fused metal copies the form of the mould into which it is cast. A cubic crystal of salt in clay, for example, is removed by percolating water, and the cubical cavity is afterwards filled with gypsum.

(4.) "*Again:* Crystals are sometimes *incrusted* over by other minerals, as cubes of fluor by quartz; and when the fluor is afterwards dissolved away, as sometimes happens, hollow cubes of quartz are left.

239. "The pseudomorphs of the first kind here mentioned are *pseudomorphs by alteration*; those of the second, *pseudomorphs by replacement;* those of the third, *pseudomorphs by infiltration;* those of the fourth, *pseudomorphs by incrustation.*

240. "These several processes are not always wholly distinct, or distinguishable in the result. It may be difficult to determine, in the case of many silicified crystals, whether there has been a gradual *replacement* of the mineral by the new material, while removal was in equal progress, as is true of petrified wood, or whether the cavity was first formed, and then the silica was *infiltrated*, It may be doubtful also, in many cases, whether the change by *incrustation* was not actually a change by *replacement* for the exterior of the original crystal, and then this process ceasing after a thin layer of new material was formed, the remaining part of the old crystal within was subsequently removed by solution. Much investigation of the subject, and as far as possible, a study of actual cases in progress, may be required, before each instance of pseudomorphism shall be referable to its place in one of the four divisions here laid down. The petrifaction of wood is a plain instance of replacement, for here every fibre of the original wood is usually copied with the utmost perfection.

241. "The process by which pseudomorphs of the first two kinds (by *alteration* and *replacement*) are produced is chemical in its nature. In the first, it depends on chemical affinities and attendant causes alone, acting either with or without water, and the water, when present,

either cold or heated. In the second, the process of solution and substitution is not less chemical. When a substance is undergoing the change of state called solution, the molecular forces are in excited action, and if any other substance is present just then passing from the liquid to the solid state, the passage of the former to the liquid state appears to aid by a transfer of force or by induction, in causing the change to a solid state in the latter, molecule for molecule, and thus the replacement is gradual and successive, and every minute striæ is copied.

242. "With regard to pseudomorphs of the last two kinds, the process is altogether mechanical. It is simply the filling of a ready made mould, or the incrusting of a model."*

243. ISOMORPHISM.—Crystals are subdivided by crystallographers into six classes or systems.† The crystals belonging to the regular system have three equal axes, cutting one another at right angles. The most important forms of this system are the cube, the regular octohedron, and rhombic dodecahedron. If a body crystallizes according to this system, it is not defined by saying it assumes the

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* Dana's "System of Mineralogy," 3rd edition. The student is referred to this work for further information on pseudomorphism; the student will find in Dana's work, and also in Phillips's "Mineralogy," a list of pseudomorphous minerals.

† We shall merely give the names and definitions of the six systems, referring the student to the more general works on chemistry for further information on crystallography.

I. REGULAR SYSTEM.

The forms of this system are characterized by three axes of equal length, intersecting at right angles.

II. THE SQUARE PRISMATIC SYSTEM.

The forms belonging to this system are characterized by three rectangular axes, two of which are equal, and the third unequal.

III. THE RHOMBOHEDRAL SYSTEM.

The forms belonging to this system are characterized by four axes, of which three are equal, and cross each other at angles of 60°; whilst the fourth is perpendicular to these, and may vary in length.

IV. THE RIGHT PRISMATIC SYSTEM.

The forms of this system are distinguished by three rectangular axes, which are all unequal.

V. THE OBLIQUE SYSTEM.

This system is characterized by three unequal axes; two of them cross each other obliquely, the third is perpendicular to both the others.

VI. THE DOUBLY OBLIQUE SYSTEM.

The forms of this system have three unequal axes, oblique, and bearing to each other indefinite relations.

regular octohedric or the cubic form; for all octohedrons and hexahedrons of the regular system are identical. The same difficulty does not exist in the other systems, for configurations of the same name, belonging to the same system, are far from being similar. If, therefore, a substance crystallizes in the regular system, it cannot be distinguished by its crystalline form, because other substances of the same crystalline form belonging to that system have the same angular measurement; and as only a comparatively small number of forms comprise the system, it happens that a great number of substances, very dissimilar in properties and chemical composition, have yet identically the same crystalline forms. But up to the year 1819 it was thought that *identity of form* in crystals belonging to the other systems indicated *identity of chemical composition*. In that year M. Metscherlich observed that certain substances had the property of assuming the same crystalline form, and that they were capable of replacing each other in the same crystals in *indefinite proportions*, when a mixed solution of these substances was submitted to the process of crystallization. He termed this similarity in crystalline forms *isomorphism* (from ισος, *like*, and μορφη, *form*) and the bodies which assume one and the same form, he named *isomorphous bodies*. The law at which he arrived is as follows:—*From an equal number of atoms, similarly combined, a crystal of like form is produced.* The crystalline form is dependent upon the number and the relative position of the atoms, and not upon their chemical nature. We shall endeavour, as we proceed, to show how far the law is confirmed.

244. The student will the more readily understand isomorphism, if we first show the behaviour of two or more non-isomorphous crystalline substances in the same solution or mixture; and afterwards the behaviour of two or more isomorphous crystalline substances under similar circumstances. If the *non-isomorphous* substances are present in the mixture in about equal proportions, and one of them is more insoluble in water, or some other liquid, at one temperature than the others, we can separate that substance, or the greater part of it, from the others, by conducting the operations of solution (if the mixture of the solids is not already dissolved), crystallization, and evaporation in accordance with this property

Or, if the substances differ but little in solubility, but one of them is present in larger quantity than the others, it is easy to perceive that in evaporating the solution, the one that is present in the largest proportion will first crystallize. Both classes of facts are illustrated in the following example:—Commercial nitrate of potash always contains variable quantities of chloride of potassium and chloride of sodium, and from these substances it must be entirely free when used in the manufacture of gunpowder. Now, 100 parts of water at 70° F. dissolves the same quantity (35 parts) of each of these salts, but 100 parts of water at 212° F. dissolves 240 parts of nitrate of potash, 35 parts of chloride of sodium, and 55 of chloride of potassium. Suppose we had some nitrate of potash containing, for every 240 parts of that salt, 30 parts of chloride of sodium, and the like quantity of chloride of potassium; if we were to dissolve it in the proportion of 300 parts of the salt to 100 of boiling water, and let this solution become cold, about 200 parts of the nitrate of potash would crystallize out, whilst the whole amount of the other two salts would remain in solution. These 200 parts of nitrate of potash would be perfectly pure, with the exception of the small quantity of mother liquor,* with which they would be moistened; to free the crystals from this contamination they may be washed with a small quantity of cold water, or better, with a saturated solution of pure nitrate of potash.† If the mother liquor, which would contain nearly equal quantities of each of the three salts, were evaporated at 212° F., 84 parts of water out of every 100 could be evaporated, without any of the nitrate of potash being deposited, whereas the expulsion of so much water would cause 25 parts of chloride of sodium, and 22 of chloride of potassium, to separate. If the clear solution (that is, free from the chlorides which have crystallized out), when it has reached this degree of concentration, were drawn off into another vessel and allowed to cool, a further crop of crystals of nitrate of potash, nearly pure, would be obtained; they might easily be rendered perfectly pure by washing them in the way just stated. The operation of crystallization is, therefore, frequently had recourse to, both in the manufactory and the laboratory, in the purification of crystalline bodies.

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* The liquor from which the crystals have separated.

† After water has been saturated with one substance, although it cannot dissolve a further quantity of that one, it can still dissolve other substances.

245. If, however, the different crystalline *non-isomorphous* substances which composed the mixture were of equal, or nearly equal solubility, and were present in about equal proportions, although they could not well be separated from each other by crystallization, still, on evaporating the liquid, *the crystals obtained would not consist of a mixture of each of the substances*, but we should obtain *separate crystals of each substance*, which, if sufficiently large, would be distinguished by the naked eye, or, at all events, with the aid of the microscope.

246. But with *isomorphous* bodies the case is different. On evaporating a solution containing two or more of these bodies, *they do not generally crystallize separately, but every individual crystal contains a quantity of each substance;* yet the substances do not chemically unite with each other, for the quantity of each substance entering into the crystal is quite indefinite; "they are mixed together mechanically in the crystals, and hence the form of the actual crystal is intermediate between those which the separate bodies would have had if they were pure. In order that bodies may so crystallize together, it is not only nécessary that they should be of the same crystalline system, but the crystalline forms must resemble one another very closely in all their angles and sides. Thus, not only will iodide of potassium and sulphate of soda, which belong to different systems of crystallization, not crystallize together; but glauber salt and carbonate of soda, which do belong to the same system, will not crystallize together, because, the relations of their angles and sides being completely different, they cannot mix together so as to form an uniform solid. But sulphate of zinc and sulphate of magnesia belong not merely to the same crystalline system, but they are almost identical in their figures; the eye cannot make any distinction between their crystals; and hence, when a crystal is being formed in a solution containing these two bodies, the molecular and crystalline forces being the same for both, they concur in the building of the crystal without interfering with each other. Hence, as there is a very

small difference between the angles of the rhombic prisms of the two salts, the one being 90° 30′, and the other 91° 8′, if they be mixed in equal proportions in the crystal, its angle must be 90° 49′. Carbonate of lime and carbonate magnesia are, like the sulphates of zinc and magnesia, almost identical in crystalline form, and they exist in nature mixed together, forming the dolomite or magnesian limestone. The quantity of carbonate of lime is to the quantity of carbonate of magnesia as 50·6 to 42·8; and as the angle of the rhomb of carbonate of lime is 105° 4′, and that of carbonate of magnesia is 107° 40′, the angle of the mixed crystal is found by multiplying the angle of each constituent by its quantity, adding these products together, and dividing by the quantity of the mixture; and the result is 106° 15′, the angle of the rhombic crystal of magnesian limestone.

247. "The peculiarity of crystallization which isomorphous bodies possess, may be illustrated in another manner. Ordinary alum is a sulphate of alumina and potash; but there are a great variety of other double sulphates which crystallize in the same form, and which constitute a well-defined crystalline genus. If an octohedral crystal of common alum be placed in a solution of the sulphate of alumina and ammonia, the crystal augments in size by the addition of the layers of that salt. If it be then removed to a solution of sulphate of potash and peroxide of iron, it acquires another layer; by a solution of sulphate of ammonia and peroxide of iron, another still; and by means of the solution of the alums which consist of oxide of chrome united to potash or ammonia, with sulphuric acid, the crystal may grow to a still greater size. The chemical constituents of the crystal may thus vary, but it retains its form; the number of equivalents of chemical substances contained in it remains also the same, although they may not remain identical in nature. The potash and ammonia on the one hand, the oxide of iron, the alumina, and the oxide of chrome upon the other,* agree in producing

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* The general formula for the alums is $M_2O_3, 3SO_3 + MO, SO_3 + 24$ aq.; the M_2O_3 represents any of the following isomorphous oxides:—alumina, sesquioxide of chromium, sesquioxide of iron, sesquioxide of manganese. The MO represents potash, soda, or oxide of ammonium.

the same crystalline arrangement of particles, in impressing upon their compounds, with the same bodies, the same crystalline form."[*]

248. If a considerable difference in solubility exists between the isomorphous bodies, they may be separated in a great measure by crystallization. Examples.—The two isomorphous salts, permanganate and perchlorate of potash, will crystallize apart on account of the difference in the solubility of these two salts; and potash alum may be separated in a great measure from iron alum by crystallization, as the iron alum is more soluble, and remains dissolved in the liquid. But most isomorphous salts, when once dissolved together, do not crystallize apart. Examples.—When a solution of iodide of potassium, to which a little chloride of potassium has been added, is evaporated to the crystallizing point, the crystals contain chloride of potassium as well as iodide of potassium; iodide of potassium cannot be separated by crystallization from chloride of potassium. Sulphate of copper cannot be separated by crystallization from sulphate of the protoxide of iron; however frequently we re-crystallize the substance, the crystals will always contain, throughout their whole mass, iron as well as copper. But if we change the protoxide of iron into sesquioxide—as, for example, by the action of chlorine—we shall then obtain pure crystals of sulphate of copper; it is only in this way that we can free, by crystallization, sulphate copper from iron.[†]

249. "The same intermixture of isomorphous substances which takes place in artificial salts is found to occur in minerals, and affords a luminous explanation of the great variety both in the kind and proportion of substances which may coexist in a mineral species, without its external character being thereby essentially affected. Thus, garnet is a double silicate of alumina and lime, expressed by the formula $(Al_2 O_3 + Si O_3) + 3$

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[*] Sir R. Kane's "Elements of Chemistry," 2nd edition.

[†] Although Mitscherlich has the merit of first recognising isomorphism in a sufficient number of cases to prove its generality, Gay Lussac first observed the fact that a crystal of potash alum, when transferred to a solution of ammonia alum, continued to increase without its form being modified; Beudant was the next to observe it, with regard to sulphate of copper and sulphate of protoxide of iron.

$(CaO + SiO_3)$; but in garnet, as in alum, the alumina may be replaced by peroxide of iron, yielding the compound $(Fe_2O_3 + SiO_3) + 3\,(CaO + SiO_3)$, or they may be both present in any proportion, provided that their sum is equivalent to either singly. So, while peroxide of iron displaces the alumina, the lime may be exchanged for protoxide of iron; and a mineral would result $(Fe_2O_3 + SiO_3) + (3\,FeO + SiO_3)$, which contains neither alumina nor lime, though it has still the form of garnet. Instead of protoxide of iron, the lime may be replaced by magnesia, protoxide of manganese, or any other isomorphous base; or any equivalent quantity of some or all of these may take the place of the lime, without the crystallographic character being destroyed. In like manner, epidote is a double silicate of alumina and lime, expressed by $(Al_2O_3 + SiO_3) + (CaO + SiO_3)$; and here again varieties of epidote are to be expected, in which alumina and lime are replaced, partially or wholly, by an equivalent quantity of isomorphous bases."

250. The simple bodies which are known to crystallize are,—

Regular System.
Carbon* Gold
Phosphorus Platinum
Selenium Mercury
Copper Titanium
Silver Lead.

Rhombohedral.
Carbon† Arsenic
Tellurium Antimony
Tin Bismuth Zinc

Right Prismatic.
Sulphur Iodine

Oblique Prismatic.
Sulphur.

251. The following table exhibits some of the more important of the groups in which the existence of isomorphism has been distinctly ascertained:—

GROUP I.

Alumina	Al_2O_3	The first four members of this group are isomorphous in the *separate* state. Mn_2O_3 is isomorphous with the first three members when in
Sesquioxide of Chromium	Cr_2O_3	
Sesquioxide of Iron	Fe_2O_3	
Ilmenite	$FeTiO_3$	
(Sesquioxide of Manganese)	Mn_2O_3	

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* As diamond. † In graphite, as it separates from cast iron when fused.

combination; these sesquioxides, combined with sulphuric acid, with one of the alkaline sulphates, and with water, form, as we have seen, the different species of alum, which have all the octohedral form.

Group II.

Arsenious Acid $As O_3$ } The elements arsenic and
Teroxide of Antimony, $Sb O_3$ } antimony are isomorphous;
their two oxides, $As O_3$ and $Sb O_3$, are each of them dimorphous, and they are isomorphous in each form. The corresponding sulphides of these oxides are also isomorphous; for example, $3 Ag S, As S_3$ (light-red silver), and $3 Ag S, Sb S_3$ (dark-red silver), both belong to the rhombohedral system.*

Group III.

Antimonides } The arsenide ($Ni_2 As$) and antimonide
Arsenides } ($Ni_2 Sb$) of nickel are isomorphous. Two
Sulphides } atoms† of sulphur are isomorphous with one
atom of arsenic and one of antimony, as $Fe_2 S_4$ and $Co_2 As S_2$; also $Fe_2 S_4$ and $Fe_2 As S_2$.

Group IV.

Titanic Acid $Ti O_2$ } are isomorphous in the separate
Binoxide of Tin, $Sn O_2$ } state, as rutile ($Ti O_2$) and tin-
stone ($Sn O_2$) have the same form, although Ti and Sn crystallize in different forms.

Group V.

Chloride of Potassium, $K Cl$ }
Iodide of Potassium $K I$ } These potassium compounds
Bromide of Potassium, $K Br$ } are isomorphous.
Fluoride of Potassium, $K F$ }

Group VI.

Phosphoric Acid, $P O_5$ } The salts of these acids are iso-
Arsenic Acid $As O_5$ } morphous.
These acids form different classes of salts by combining with bases in different proportions, and the isomorphism of the arseniates and phosphates of each class is complete. Examples:

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[*] Sulphide of bismuth ($Bi S_3$) is isormorphous with $As S_3$ and $Sb S_3$; and antimony displaces bismuth in kobellite, needle-ore, &c. Bismuth itself is paramorphous with arsenic and antimony.

[†] If we adopt 32 as the eq. of S., then one atom of that element is isomorphous with one of As and one of Sb.

Square prismatic system.—$NH_4O, 2HO, PO_5$,—$NH_4O, 2HO, AsO_5$,—$KO, 2HO, PO_5$,—$KO, 2HO, AsO_5$. *Right prismatic system.*—NaO, PO_5, 4 aq.—NaO, AsO_5, 4 aq. *Oblique system.*—$2NH_4O, PO_5, HO$,—$2NH_4O, AsO_5, HO$: $2NaO, PO_5$, 25 aq.—$2NaO, AsO_5$, 25 aq.*

Group VII.

Sulphuric Acid, SO_3
Selenic Acid SeO_3
Manganic Acid, MnO_3
Chromic Acid CrO_3

The salts of these acids, when they contain the same base and the same proportion of base and of water of crystallization, have the same crystalline form. Examples: *Square prismatic system.*—NiO, SO_3 + 7 aq.—NiO, SeO_3, 7 aq.—ZnO, SeO_3, 7 aq.; $2NH_3, AgO, SO_3$—$2NH_3, AgO, SeO_3$,—$2NH_3, AgO, CrO_3$. *Right prismatic system.*—NaO, SO_3,—NaO, SeO_3,—AgO, SO_3,—AgO, SeO_3 : KO, SO_3,—KO, SeO_3,—KO, CrO_3, KO, MnO_3 : MgO, SO_3 + 7 aq.—ZnO, SO_3 + 7 aq.—NiO, SO_3 + 7 aq.—MgO, ScO_3, + 7 aq.—ZnO, SeO_3 + 7 aq. *Oblique prismatic system.*—$KO, 2SO_3, HO$,—$KO, 2SeO_3, HO$: CaO, SO_3 + 2 aq.—CaO, SeO_3 + 2 aq.—FeO, SO_3 + 2 aq. : FeO, SO_3, + 6 aq.—CoO, SO_3 + 6 aq.—MnO, SO_3, + 6 aq.—CoO, SeO_3 + 6 aq. : MgO, SO_3 + 7 aq.—ZnO, SO_3 + 7 aq.—CoO, SO_3 + 7 aq.—NiO, SO_3 + 7 aq.—MgO, SeO_3 + 7 aq.—CoO, SeO_3 + 7 aq. : NaO, SO_3 + 10 aq.—NaO, SeO_3 + 10 aq.—NaO, CrO_3 + 10 aq. *Doubly oblique prismatic system.*—MnO, SO_3 + 4 aq.—MnO, SeO_3 + 4 aq.—ZnO, SeO_3 + 4 aq.—CoO, SeO_3 + 4 aq. : CuO, SO_3 + 5 aq.—CuO, SeO_3 + 5 aq.—MnO, SO_3 + 5 aq.

Group VIII.

Chromic Acid, CrO_3
Molybdic Acid, MoO_3
Tungstic Acid, WO_3
Tantalic Acid TaO_3

CaO, WO_3,—PbO, WO_3,—PbO, MoO_3,—and PbO, CrO_3, are isomorphous; also FeO, WO_3 (Wolfram), and FeO, TaO_3 (Tantalite), are isomorphous.

Group IX.

Perchloric Acid ClO_7
Permanganic Acid, Mn_2O_7
Periodic Acid IO_7

The salts of these acids are isomorphous. One atom of chlorine in perchloric acid, or one atom of iodine in periodic acid, evidently fulfils the same function as two atoms of manganese in permanganic acid.

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* It was by the study of the forms of the corresponding arseniates and phosphates that Mitscherlich first established the principle of isomorphism.

GROUP X.

Magnesia	$Mg\,O$
Protoxide of Iron	$Fe\,O$
Protoxide of Manganese,	$Mn\,O$
Oxide of Nickel	$Ni\,O$
„ Cobalt	$Co\,O$
„ Copper	$Cu\,O$
„ Zinc	$Zn\,O$
„ Cadmium	$Cd\,O$
Lime in calc-spar	$Ca\,O$
Lead in Plumbo-calcite	$Pb\,O$

We have seen, in Group VII., that these bases, in combination with sulphuric and selenic acids, are isomorphous. Their carbonates and their combinations with the sesquioxides of Group I., are also isomorphous. Example: *Rhombohedral system.*—$Ca\,O, C\,O_2$ (Calc-spar), — $Mg\,O, C\,O_2$, — $Ca\,O, C\,O_2 + Mg\,O, C\,O_2$, — $Mn\,O, C\,O_2$, — $Zn\,O, C\,O_2$, — $Fe\,O, C\,O_2$. *Regular system.*—$Mg\,O, Al_2\,O_3$ (Spinell), — $Mg\,O, Fe_2\,O_3$ (Pleonast), — $Zn\,O, Al_2\,O_3$ (Gahnite), — $Zn\,O, Fe_2\,O_3$ (Franklinite), — $Fe\,O, Fe_2\,O_3$ (Magnetic iron ore). All the sulphates of this group are capable of forming double salts with some anhydrous sulphate *which is not isomorphous* with the group, as, for example, with sulphate of potash. The usual amount of water which the sulphates of this group contain is 7 eq. Graham found that 6 eq. of the water could be expelled at 212° F., but that the remaining 1 eq. required a much higher temperature for its expulsion, but that it may be displaced by some non-isomorphous anhydrous sulphate. Graham, therefore, called this atom of water constitutional or *saline* water. Example.—When sulphate of magnesia ($Mg\,O, S\,O_3, H\,O + 6$ aq.) and sulphate of potash are separately dissolved in water, in equivalent proportions, mixed while hot and allowed to crystallize, a double salt ($Mg\,O, S\,O_3 + K\,O, S\,O_3 + 6$ aq.) crystallizes out, having the same crystalline form as sulphate of magnesia.

GROUP XI.

Baryta	$Ba\,O$
Strontia	$Sr\,O$
Lime	$Ca\,O$
Oxide of Lead,	$Pb\,O$

The salts of these bases are isomorphous. Lime, in one of its dimorphous forms, is a member of this group. Lead and lime, in combination with the acids in Group VIII., we have already seen, are isomorphous. We shall here give examples of the isomorphism of many of the other salts of these bases. *Right prismatic system.*—$Ca\,O, C\,O_2$ (Arragonite), — $Ba\,O, C\,O_2$, — $Sr\,O, C\,O_2$. — $Pb\,O, C\,O_2$: $Ba\,O, S\,O_3$, — $Sr\,O, S\,O_3$, — $Pb\,O, S\,O_3$: $Ba\,O, C_4\,H_3\,O_3$, 3 aq. (Acetate of Baryta),—$Pb\,O, C_4\,H_3\,O_3$, 3 aq. (Acetate of Lead). *Rhombohedral system.*—$Sr\,O, S_2\,O_5 + 4$ aq. — $Ca\,O, S_2\,O_5 + 4$ aq. — $Pb\,O, S_2\,O_5 + 4$ aq. : $Ca\,Cl, 9\,Ca\,O, 3\,P\,O_5$ (Apatite),— $Pb\,Cl, 9\,Pb\,O, 3\,P\,O_5$, — $Pb\,Cl, 9\,Pb\,O, 3\,As\,O_5$. *Regular system.*—$Ba\,O, N\,O_5$,—$Sr\,O, N\,O_5$,— $Pb\,O, N\,O_5$,— $Pb\,O, N\,O_5$.

GROUP XII.

Potash $K\,O$
Ammonia, $N\,H_4\,O$
Soda $Na\,O$

"These fixed alkalies may be substituted for each other in the different species of alum. Ammonia is truly isomorphous with potash, in all its compounds, but it is only rarely that the compounds containing soda appear to have the same form. In minerals, and in some forms of alum, potash is replaced by an atom of any oxide in Group X., united with an atom of water, as hydrate of lime, or by two atoms of such compound without water."

GROUP XIII.

Platinum	$K\,Cl, Pt\,Cl_2$	The double chlorides, which are formed by the union of the chloride of one of these metals and chloride of potassium, or chloride of ammonium.
Osmium	$K\,Cl, Os\,Cl_2$	
Iridium	$K\,Cl, Ir\,Cl_2$	

252. "Graham is of opinion that water stands in an isomorphous relation with the bases of the 10th group, equivalent for equivalent. The isomorphism is certainly not proved, but the resemblance which, in a chemical point of view, water exhibits towards these bases, indicates that such is the case. Thus, according to that chemist, nitrate of copper, hydrated nitric acid of specific gravity 1·42, and sub-nitrate of copper, are expressed by the formulæ—

$$Cu\,O, N\,O_5 + 3\,H\,O$$
$$H\,O, \ N\,O_5 + 3\,H\,O$$
$$Cu\,O, N\,O_5 + 3\,(Cu\,O, H\,O)$$

Crystallized oxalic acid, or oxalate of oxide of hydrogen, corresponds with oxalate of magnesia; hydrated sulphuric acid, $HO, SO_3 + HO$, corresponds with sulphate of magnesia, $MgO, SO_3 + HO$; and this similarity, in a chemical point of view, is regarded by Graham as a main objection to the division of the equivalent of hydrogen into two atoms."

253. Scheerer has brought water into an isomorphous relation with the same bases in a totally different manner. He finds, by the analysis of a great number of minerals, that one atom of MgO, FeO, or MnO, and probably also of ZnO, NiO, and CoO, may be replaced by three atoms of water, and one atom of CuO by two atoms of water, without change of crystalline form.

254. This kind of isomorphism, which appears to play an important part in the mineral kingdom, has received the name of *Polymeric isomorphism*. It was first noticed in the minerals cordierite and aspasiolite; these two minerals crystallize in the same form, and crystals are found consisting partly of cordierite and partly of aspasiolite, the most complete transitions from one to the other occurring in the same specimen. Moreover, both minerals contain nearly the same proportions of silica and alumina; but aspasiolite contains a smaller quantity of magnesia, and a larger quantity of water, than cordierite, the difference being such, that three atoms of water in the former may be regarded as the equivalent of one atom of magnesia in the latter.

255. We must now make the student acquainted with the method for deducing the rational formula for compounds containing isomorphous constituents; and for that purpose we must first explain a method of deducing the rational formula of oxygen salts, and which also applies equally to metallic sulphides. The method consists in ascertaining the ratio which the quantities of oxygen in the different constituents bear to each other. Example:—The salt called phosphate of magnesia and ammonia, has the following per-centage composition:—

Magnesia - - - - - -	16·30	
Oxide of ammonium - - -	10·60	
Phosphoric anhydride (PO_5) - -	29·09	
Water - - - - - - -	44·01	
		100·00

256. To find the rational formula of this salt, in the way stated, we have to ascertain the amount of oxygen in the per-centage amounts of each of its four constituents. We ascertain this by simple rule of three: for, 1st, we know the atomic weights of these substances; 2nd, we know the quantity of oxygen contained in an atom of each of these substances; 3rd, we know the quantity of each of these substances in 100 parts of the salt; and from these three terms we find the 4th, viz., the quantity of oxygen in the per-centage amounts of each of these four substances. Having obtained the respective quantities of oxygen, we reduce the quantities to the simplest expression, from which we deduce the formula. Example:—

20 of MgO	contain	8 of O,	consequently	16·30 of MgO	contain	6·52 of O
26 of NH_4O	„	8 of O,	„	10·60 of NH_4O	„	3·26 of O
71·76 of PO_5	„	40 of O,	„	29·09 of PO_5	„	16·30 of O
9·0 of HO	„	8 of O,	„	44·01 of HO	„	39·12 of O

The respective quantities of oxygen are, therefore,—

3·26 : 6·52 : 16·30 : 39·12

These proportions, reduced to their simplest expression, give—

1 : 2 : 5 : 12

which leads to the formula—

$$2\,MgO, NH_4O, PO_5 + 12\,HO$$

257. We have already noticed the fact that isomorphous substances can replace each other in all proportions. They are consequently calculated as *one* substance, in determining the formula of the compound containing them. Example.—A specimen of Bohemian garnet was found to have the following per-centage composition:—

Silicic acid	40·00		21·19
Alumina	28·50	13·30	18·94
Sesquioxide of iron	16·50	4·95	
„ „ manganese	0·25	0·07	
„ „ chromium	2·00	0·62	
Magnesia	10·00	4·00	5·00
Lime	3·50	1·00	
	100·75		

The ratio between 5·00 : 18·94 : 21·19
is as - - - 1· : 3·78 : 4·23;

for which we may safely substitute 1 : 3[*] : 4

Designating one equivalent of the metal by M, we find from these numbers the formula,—

$$\mathrm{M\,O + M_2\,O_3 + 4\,Si\,O_3}$$
$$\mathrm{or,\ M_2\,O_3,\ 3\,Si\,O_3 + M\,O,\ Si\,O_3}$$

which may be written in detail thus:—

$$\left.\begin{matrix}\mathrm{Al_2}\\ \mathrm{Fe_2}\\ \mathrm{Mn_2}\\ \mathrm{Cr_2}\end{matrix}\right\}\mathrm{O_3,\ 3\,Si\,O_3} + \left.\begin{matrix}\mathrm{Mg}\\ \\ \mathrm{Ca}\end{matrix}\right\}\mathrm{O,\ Si\,O_3}$$

258. "Besides isomorphous substances, all bodies of analogous composition possess the faculty of replacing each other in compounds. Thus we find that $\mathrm{K\,O}$, $\mathrm{Na\,O}$, $\mathrm{Ca\,O}$, $\mathrm{Mg\,O}$, &c., replace each other. These substances, likewise, must be expressed *collectively* in the formula."

259. We will here notice a system of notation which, although not much used by chemists, is employed in most mineralogical works. In this system, oxygen is expressed by points placed over the symbol of the body with which it is in combination, each point representing an atom of oxygen. For example:—the symbol for carbonic acid, by this system, is $\ddot{\mathrm{C}}$. Each atom of sulphur is indicated by a comma[†] placed over the symbol of the substance with which the sulphur is in combination; and the atoms of hydrogen are indicated by points placed under the symbol of the body with which it is in combination. All the other elements are expressed by the usual symbols; and a stroke through or under the symbol indicates two equivalents of the element. For example,—the symbol for two equivalents of aluminum is $\underline{\mathrm{Al}}$, or $\sout{\mathrm{Al}}$; and for alumina, $\overset{\cdots}{\sout{\mathrm{Al}}}$, or $\overset{\cdots}{\underline{\mathrm{Al}}}$. By this system, Bohemian garnet would be formulated thus:—

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[*] Four would be nearer 3·78 than 3; but we have to take into account the excess obtained by the chemist who made the analysis; and therefore, for this and other reasons, the proportion of the sesquioxide is more likely to be 3 than 4.

[†] Sometimes strokes are used in place of commas for sulphur; the strokes leaning from right to left.

$$\overbrace{\underline{\mathrm{Al}}\;\underline{\mathrm{Fe}}\;\underline{\mathrm{Mn}}\;\underline{\mathrm{Cr}}}^{\cdots}\;3\,\dddot{\mathrm{Si}}+\overbrace{\mathrm{Mg}\;\mathrm{Ca}}^{\cdot}\;\dddot{\mathrm{Si}}$$

EXERCISES.

122. Deduce from the following per-centage numbers the formulæ of the different substances, and employ the system of notation just explained :—

123. A specimen of the mineral monradite was found to contain, in 100 parts, SiO_3 56·17, of MgO 31·63, of FeO 8·56, HO 4·04.

124. A specimen of the mineral prehnite was found to contain, in 100 parts, CaO 26·28, Mn_2O_3 0·15, Fe_2O_3 6·81, Al_2O_3 19·30, SiO_3 43·03, HO 4·43.

125. A specimen of the mineral zoisite was found to contain, in 100 parts, CaO 18·85, MnO 7·55, FeO 4·24, Al_2O_3 29·83, SiO_3 40·03.

126. A specimen of ferruginous zinc-spar was found to contain, in 100 parts, ZnO, CO_2 71·08, FeO, CO_2 23·98, MnO, CO_2 2·58, CaO, CO_2 2·54.

127. A specimen of the mineral andesine was found to contain, in 100 parts, SiO_3 59·60, Al_2O_3 24·28, Fe_2O_3 1·58, CaO 5·77, MgO 1·08, NaO 6·53, KO 1·08.

128. A specimen of the mineral ullmannite was found to contain, in 100 parts, As 11·75, Sb 47·75, S 15·25, Ni 25·25.

129. A specimen of the mineral kobellite was found to contain, in 100 parts, S 17·86, Sb 9·24, Bi 27·05, Pb 40·12, Fe 2·96, CuO ·80, gangue* 1·45.

130. A specimen of obsidian was found to contain, in 100 parts, SiO_3 69·46, Al_2O_3 2·60, Fe_2O_3 2·60, CaO 7·54, MgO 2·60, KO 7·12, NaO 5·08, HO 3·00.

131. A specimen of the mineral cordierite was found by Scheerer to contain, in 100 parts, SiO_3 50·44, Al_2O_3 32·95, MgO 12·76, CaO 1·12, FeO 0·96, MnO a trace, HO 1·02.

132. A specimen of the mineral aspasiolite was found by Scheerer to contain, in 100 parts, SiO_3 50·40, Al_2O_3 32·38, MgO 8·01, CaO trace, FeO 2·34, MnO trace, HO 6·73.†

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* As the gangue is not a part of the mineral, it must, of course, be omitted in the calculation.

† When the student has completed exercises 131 and 132, he ought again to read pars. 253 and 254.

260. The method adopted for formulating compounds containing several isomorphous constituents, may appear to the student to be at variance with the indivisibility of atoms; for example, the formula, $\left.\begin{matrix}Fe\,O\\Mn\,O\\Mg\,O\end{matrix}\right\}C\,O_2$, designates, according to the strict meaning, a combination of one atom of $C\,O_2$, united with the fraction of an atom of each of the three bases; but this formula is only an abbreviation of the following:—$\left\{\begin{matrix}m\ Fe\,O,\ C\,O_2\\n\ Mn\,O,\ C\,O_2\\o\ Mg\,O,\ C\,O_2\end{matrix}\right.$ in which *m*, *n*, and *o*, indicate the number of atoms of each carbonate which are united together; and these numbers are not constant, but *variable*. In each different specimen of the compound, these numbers may vary; in fact, this variability is one of the peculiarities of the displacement which takes place between isomorphous bodies.

261. In proceeding to lay before the student the different reasons which have been suggested for the explanation of the phenomena of isomorphism, we must first draw his attention to the fact "that similarity of chemical constitution does not follow from similarity of form.' For example:—Copper pyrites ($Cu\,Fe\,S_2$) and braunite ($Mn_2\,O_3$) have the same form; arragonite ($Ca\,O,\ C\,O_2$) and nitrate of potash ($K\,O,\ N\,O_5$) have the same form; quartz ($Si\,O_3$) and chabasite ($Al_2\,O_3,\ 2\,Si\,O_3 + Ca\,O,\ Si\,O_3 + 6\,aq.$) have the same form; bisulphate of potash ($K\,O,\ S\,O_3 + H\,O,\ S\,O_3$), in one of the two forms in which it can crystallize, has the same form as sulphur, one of its elements. When bodies are so dissimilar in chemical constitution, though similar in form, they cannot possibly replace, or be substituted for one another. Quartz, for instance, can never take the place of the more complex compound chabasite, and nitrate of potash can never take the place of carbonate of lime; and therefore isomorphism cannot, as the term would imply, depend simply upon similarity of form. The substances which are truly isomorphous must correspond in other properties besides external form. The crystalline form cannot therefore be dependent, as Mitscherlich stated, upon the number and arrangement of the atoms; for although, as we have seen, bodies which have a similar chemical constitution,

have also a similar crystalline form. yet we have also seen that bodies which have very different chemical constitutions, may have the same crystalline form. But even bodies which are truly isomorphous, do not always consist of an equal number of elementary atoms. The isomorphism of Ni S or Ni S_2, and Ni_2 As and Ni_2 Sb, is usually quoted as one of the examples; but if we adopt the new equivalents (115), these formulæ become concordant, as the formula of sulphide of nickel would then be Ni_2 S. The perchlorates and permanganates may be substituted for each other in crystals, without producing any change of form; they are therefore truly isomorphous: but in permanganic acid, two equivalents of manganese are united with seven equivalents of oxygen; whilst in perchloric acid, only one equivalent of chlorine is united with seven equivalents of oxygen, and therefore, if we had no other example, this would be sufficient to prove that isomorphous bodies do not always contain an equal number of elementary atoms. It must here be remarked that Berzelius regarded the isomorphism of perchlorate and permanganate of potash, as the most decided reason for halving the equivalent of chlorine (114), and consequently, also, of bromine, iodine, &c.; for as permanganic acid consists of two equivalents of manganese and seven of oxygen, and as perchlorate of potash is isomorphous with permanganate of potash, Berzelius considered that it necessarily followed that perchloric acid must consist of two equivalents of chlorine and seven equivalents of oxygen; but if the student will refer to paragraph 115, he will see that, according to the most recent ideas, if the atomic weights of chlorine, bromine, iodine, &c., are halved, the atomic weights of the metals must also be halved. The isomorphism of ammonia, a compound consisting of five elementary atoms, with the elementary body potassium,* is another striking example that isomorphous bodies do not always contain an equal number of elementary atoms; and therefore the view that Mitscherlich first entertained, viz., "that the crystalline form of a body is dependent upon the number of elements of which the body is made up," is disproved by these well-established facts.

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* It is very probable that the complex ammonias will also be isomorphous with the element potassium. It has already been found that the alkaloids quinine and conine can be substituted for potassium, ammonium, or sodium, in alums.

The isomorphism of three atoms of water with several of the oxides of Group X., and the isomorphism of two atoms of water with one atom of oxide of copper (253), might also be adduced.

262. Another view which has been advanced to explain the isomorphism of bodies is that the replacing elements themselves are isomorphous; and therefore, the crystalline form is not altered by the replacement. As the majority of the elements have not been obtained in a crystalline state, and of those which have been so obtained the majority crystallize according to the regular system, the examples must necessarily be few in which the replacing elements of two or more isomorphous compounds have each been obtained in the crystalline state, but all the facts *which are known* prove that the isomorphism of compounds is not based upon the isomorphism of the varying element; and consequently, the isomorphism of the elements cannot be inferred from the isomorphism of the compounds. Example.—We do not know whether anhydrous phosphoric, and arsenic acids have the same form, but the elements, phosphorus and arsenic, have not, as the former crystallizes in the regular, and the latter in the rhombohedral system.

263. The angles of the crystals of isomorphous substances are not always *exactly* equal,* but occasionally differ two or even three degrees; but this might even have been anticipated, for we know that by heat and other varying conditions, the angles of crystals are sensibly affected, and Mitscherlich has shown that the angles in different specimens of the same salt may vary to a considerable extent. Kopp considers that *isomorphous bodies have the same equivalent volume,*† or, in other words, that in isomorphous bodies the specific gravities stand in the same relations as the equivalent weights; and that the variation in the angles of isomorphous bodies is due to the atoms of the isomorphous bodies not *exactly*

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* As isomorphism implies that the angles are truly equal, it was proposed to indicate *approximate* forms by the term *plesimorphism* (πλησιος near); but the term has never come into use.

† The equivalent or atomic volumes of gaseous bodies have already been treated of: the equivalent volumes of solid and liquid bodies will form the subject of a future chapter.

filling the same space; consequently, the crystalline form will not be affected by the replacement of one isomorphous body by another, provided the atomic volume of the replacing body is the same as that of the body being replaced; but if the atomic volumes of the two bodies differ, the difference in volume will cause a difference in the form of the crystal. He has shown that many of the elementary bodies may be arranged in groups, each group consisting of members in which the atomic volume is identical. Example:—

	Equiv. Vol.		Equiv. Vol.
Cobalt	45	Sulphur	101
Copper	44	Tin	101
Iron	44	Arsenic	105
Manganese	44	Lead	114
Nickel	44	Gold	128
Iridium	57	Silver	128
Osmium	57	Tellurium	128
Palladium	57	Lithium	136
Platinum	57	Calcium	158
Titanium	56	Phosphorus	211
Zinc	58	Strontium	216
Aluminum	66	Antimony	222
Chromium	66	Bismuth	270
Molybdenum	66	Bromine	320
Tungsten	66	Chlorine	320
Cadmium	81	Iodine	320
Magnesium	86	Sodium	295
Mercury	91	Potassium	562
Selenium	103		

264. If, as Kopp believes, "the identity of atomic volume caused the isomorphism of bodies, then there should be no isomorphism unless the atomic volumes were the same, and all bodies with the same atomic volume should be isomorphous." Although the atomic volumes of many of the isomorphous bodies are identical, yet we see by the table it is not the case with all; for example,—the atomic volume of magnesium is 86; that of cadmium is 81; that of zinc 58; and that of iron, copper, &c., 44; yet we have seen that many of the compounds (Group X.) of these elements are isomorphous; but even these isomorphous compounds have not

the same atomic volume, the atomic volume of sulphate of copper is 280; whilst the atomic volume of sulphate of zinc is 293; again, the atomic volume of carbonate of cadmium is 232; whilst that of carbonate of iron, or carbonate of manganese, is 195; we might adduce many more examples, but these are sufficient to show that the atomic volumes of isomorphous bodies are not always identical. Again, some bodies have the same atomic volume, but not the same form; for example, carbonate of iron, oxide of silver, sulphate of cadmium, and peroxide of iron, none of which bodies have any isomorphous connection, have yet the same atomic volume.

265. Attempts have been made, when the crystalline form corresponds, but the chemical constitution differs, to harmonize them by altering the atomic weights of some of the bodies. "The following is one of the most remarkable instances of this kind:—$Ca\,O, CO_2$, as arragonite, is isomorphous with nitre (KO, NO_5) in its usual form; $Ca\,O, CO_2$, as calc-spar, with KO, NO_5 as it is sometimes obtained, and with $Na\,O, NO_5$ as it always crystallizes. Hence, $Ca\,O, CO_2$ in its two conditions, is isomorphous with KO, NO_5 in its two conditions. For this reason, Count Schaffgotsch halves the atomic weights of potassium and nitrogen; nitre then becomes $= KNO_3$. This agrees with $Ca\,O, CO_2 = Ca\,CO_3$; in both compounds, three atoms of oxygen are combined with one atom of metal and one atom of either carbon or nitrogen. This halving of the atomic weight of potassium involves the halving of those of ammonium (NH_4), sodium, silver, and gold, because potash is isomorphous with oxide of ammonium ($NH_4\,O$) and soda, and the last of these with oxide of silver; and because silver, in combination with the most various quantities of gold, always crystallizes in the same form, a circumstance which indicates the isomorphism of these two metals. The halving of the atomic weight of silver had before been proposed by H. Rose, because in grey copper ore one atom of silver takes the place of two atoms of copper, and the crystalline form of $Ag\,S$, as well as that of $Cu_2\,S$, belongs to the regular system. According to this view, the atomic weights of N, H, K, Na, Ag, and Au, would be reduced to one-half of the values now assigned to them; potash would be

K_2O, soda Na_2O, oxide of silver Ag_2O, and suboxide of silver Ag_4O. By halving the atomic weights of potassium and chlorine the similar forms of KO, ClO_7, and BaO, SO_3 would also be explained, for the composition would then be $KClO_4$ and $BaSO_4$."* Numerous facts are opposed to Schaffgotsch's hypothesis, and therefore no value is attached to it.

266. Before directing the attention of the student to the value of isomorphism in determining equivalent numbers, we will briefly bring before his notice the points at which we have arrived.

1. We have seen that some bodies are similar in crystalline form, and similar in chemical constitution and properties; bodies which are thus alike in form and constitution can replace each other in indefinite proportions. These isomorphous bodies, as we have seen, are not always made up of the same number of elementary atoms.

2. We have seen that some bodies are similar in crystalline form, but unlike in chemical constitution and and properties; bodies which are alike in form but unlike in chemical constitution cannot, as far as our knowledge at present extends, replace one another in indefinite proportions.

3. We find that many bodies which are not generally considered isomorphous, but which are analogous in chemical constitution, possess the property of replacing each other in compounds (258).

267. It is probable that, just as the allotropic state of elementary bodies, according to Brodie's experiments (193), is due to those substances possessing a different atomic number in this state to what they possess in their ordinary state, so the dimorphism of bodies may be due to the same cause; and possibly many of the substances which are similar in form, but which at present are not considered to have a similar chemical constitution, may be made to harmonize in the latter respect in the same way. This idea is supported, I think, by Scheerer's discovery (253), that two atoms, and sometimes three atoms, of water are isomorphous with one atom of the oxides forming Group X.

268. *The aid derived from isomorphism in determining*

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* "Gmelin's Handbook of Chemistry," vol. i.

equivalents will be best understood by the following examples. Not long ago, only two oxides of chromium were known; they have the following composition:—

In the first oxide, every 18·7 parts of chromium are united with 8 of oxygen.

In the second oxide, every 18·7 parts of chromium are united with 16 of oxygen. Now the atomic constitution of the first was determined to be not the protoxide, but the sesquioxide, because it was found to be isomorphous with sesquioxide of iron; the second oxide (chromic acid) became, therefore, the teroxide; and this view of the composition of this oxide was beautifully confirmed by the discovery that chromic acid was isomorphous with manganic and sulphuric acids. Since this view was taken of the constitution of these two oxides, another oxide of chrome has been discovered, which contains two-thirds less oxygen than chromic acid; therefore, if in the latter compound three equivalents of oxygen are united with one of chromium, this new oxide must be the protoxide of chromium, which is proved to be the case by its yielding salts isomorphous with the salts of protoxide of iron, &c. In like manner, alumina is regarded as the sesquioxide of aluminum, because it is isomorphous with sesquioxide of iron.*

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* The student, after he has finished this chapter, is recommended to study the chapters on Isomorphism, Dimorphism, Allotropism, and Isomerism, in Kane's "Elements of Chemistry," 2nd edit.

CHAPTER VI.

ATOMIC WEIGHTS OF THE ELEMENTS. THE CONSTITUTION OF COMPOUND BODIES. THE MEANING OF CHEMICAL FORMULÆ.

Classification of the elements, 269. *Equivalents*, 271. *Atomic weights*, 276. *Arguments for doubling the atomic weight of oxygen, &c.*, 282. *Arguments against doubling the atomic weight of oxygen, &c.*, 330. *The different views which have been and are held on the constitution of compounds*, 338. *The unitary system*, 358. *Williamson's reasons for considering that many bodies are formed on the type of water*, 373. *The different views which have been and are held on the constitution of the alcohols and ethers, and the different theories of etherification*, 374. *The different views which have been and are held on the constitution of ammonia*, 396. *Double decomposition regarded as the type of chemical action in general*, 419. *The meaning of formulæ*, 420. *The same body can have more than one rational formula*, 422. *Molecular types*, 426. *Equivalent values of radicals*, 438. *Equivalent notation*, 446. *Conjugate radicals*, 447. *Gerhardt's system of classification*, 451. *Table of the classification of bodies according to their chemical functions.*

269. *Classification of the elements.*—The elements are usually divided into two classes, metals and metalloids; this division is the one which was adopted in the infancy of the science, and is still generally continued, more on account of its simplicity and convenience than its correctness; in the following table they are distributed into the most natural families or groups. In many instances, these natural relations between the individual elements thus grouped together are very striking, in others they are more obscurely marked, and in the case of the metals of the earths proper, as well as of the noble metals, the natural affinities of these elements with the others are as yet very incompletely known.

TABLE OF THE ELEMENTS.

F	Fluorine	19·0
Cl	Chlorine	35·5
Br	Bromine	80·0
I	Iodine	127·0
O	Oxygen	16·0
S	Sulphur	32·0
Se	Selenium	80·0
T	Tellurium	128·0
N	Nitrogen	14·0
P	Phosphorus	31·0
As	Arsenic	75·0
Sb	Antimony (*Stibium*)	120·0
Bi	Bismuth	208·0
C	Carbon	12·0
Si	Silicon	28·5
Ti	Titanium	48·5
Sn	Tin (*Stannum*)	118·0
Ta	Tantalum	138·0
Bo	Boron	11·0
H	Hydrogen	1
Li	Lithium	7·0
Na	Sodium (*Natrium*)	23·0
K	Potassium (*Kalium*)	39·0
Rb	Rubidium	85·3
Cs	Cæsium	123·4
Ca	Calcium	20·0
Sr	Strontium	44·0
Ba	Barium	68·5

G	Glucinum	4·7
Y	Yttrium	32·0
Th	Thorium	59·5
Mg	Magnesium	12·0
Zn	Zinc	32·5
Cd	Cadmium	56·0
Hg	Mercury (*Hydrargyrum*)	100·0
Pb	Lead (*Plumbum*)	103·5
Ag	Silver (*Argentum*)	118·0
Cr	Chromium	26·3
Mn	Manganese	27·0
Fe	Iron (*Ferrum*)	28·0
Ni	Nickel	29·5
Co	Cobalt	29·5
Cu	Copper (*Cuprum*)	31·7
Al	Aluminum	13·7
Zir	Zirconium	33·6
Ce	Cerium	46·0
La	Lanthanum	46·0
D	Didymium	48·0
U	Uranium	60·0
Mo	Molybdenum	48·0
Vd	Vanadium	68·5
W	Tungsten (*Wolfram*)	92·0
Au	Gold (*Aurum*)	197·0
Ro	Rhodium	52·0
Ru	Ruthenium	52·0
Pd	Palladium	53·0
Pt	Platinum	98·5
Ir	Iridium	98·5
Os	Osmium	99·5

270. We shall now very briefly describe some of the chief chemical relationships which exist between the members of the first four groups.

1. *The chlorine class, or halogen group.*—The four elements constituting the members of this group "have one marked property in common, a property not pertaining to any other element with which we are acquainted—namely, that of uniting with hydrogen in the proportion of atom to atom, gaseous atomic volume to gaseous atomic volume. The combinations, moreover, take place without any condensation; while the resulting compounds are powerful acids, and exhibit a striking general resemblance in their properties. They are all gaseous, all condensible, all fuming, all soluble in water, and all result from similar reactions. Chlorine, bromine, and iodine, present a marked similarity and gradation of properties. Fluorine is separated from the other members of the group by certain specialities." The properties of bromine are intermediate between those of chlorine and iodine; its atomic weight and vapour-density are about the mean of the atomic weights and vapour-densities of chlorine and iodine (215—3); it is a liquid at the ordinary temperature, whilst chlorine is a gas, and iodine a solid; even its colour is intermediate between the other two. These three bodies are also isomorphous throughout their whole combinations. They all three unite with oxygen, in several proportions, forming corresponding oxides; but no oxygen compound of fluorine has yet been discovered. They all four form, with the metals, compounds analogous to sea-salt, and have been termed *halogens*, or salt-producers (from ἅλς, "the sea.")

2. *The sulphur group.*—Sulphur, selenium, and tellurium, exhibit the closest chemical relationship; they all unite with hydrogen in the proportion of one to two atoms, one atomic volume to two atomic volumes. These hydrogen compounds occupy two volumes, they are gaseous bodies, and possess feebly acid characters. Their oxygen compounds, or anhydrides, also correspond in composition and properties.

$$\begin{array}{lll} SO_2 & SeO_2 & TeO_2 \\ SO_3 & SeO_3 & TeO_3 \end{array}$$

The lower oxides are volatile, whilst the higher ones are decomposed at a red heat, with liberation of oxygen. We have already seen that the sulphates, seleniates, and telluriates, are isomorphous. The properties of selenium are intermediate between those of sulphur and tellurium; its atomic weight, its specific gravity, and its fusing point, are about the mean of atomic weights. specific gravities, and fusing points of the other two (215—3). Selenium has a slightly metallic appearance, whilst tellurium, on account of its metallic lustre, is frequently classed amongst the metals.

Oxygen manifests a general resemblance to the other three members of the group; it appears to occupy towards them the same relation that fluorine bears to the other members of the halogen group. "Oxygen has not yet been connected with the other three members by a certain isomorphism of any of its compounds; but a close correspondence between it and sulphur appears, in their compounds with one class of metals, being alkaline bases of similar properties, forming the two great classes of oxygen and sulphur bases, such as oxide of potassium, and sulphide of potassium; and in their compounds with another class of elements, being similarly acids, giving rise to the great classes of oxygen and sulphur acids, such as arsenious and sulpharsenious acids. They further agree in the analogy of their compounds with hydrogen, particularly of binoxide of hydrogen, and bisulphide of hydrogen, both of which bleach, and are remarkable for their instability; and in the analogy of the oxide, sulphide, and telluride of ethyl, and of alcohol and mercaptan, which last is an alcohol with its oxygen replaced by sulphur."*

3. *Phosphorus class.*—Nitrogen, phosphorus, arsenic, and antimony, each combine with three atoms of hydrogen, the compound produced occupying two volumes; none of the other elements are capable, so far as our knowledge extends, of forming terhydrides. No hydrogen compound of bismuth has yet been formed, but it forms with chlorine a terchloride. The terhydrides of nitrogen, phosphorus, arsenic, antimony, are, in a greater or less degree, basic in character. The hydrogen compound of nitrogen has long been named ammonia; but ammonia is now beginning to be used more as a generic than a specific name, as recent

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* Odling's "Manual of Chemistry."

researches have proved that phosphorus, arsenic, and antimony, can occupy the place of the nitrogen in the ammonia series. The atomic weight of arsenic is about the mean of the atomic weights of phosphorus and antimony. We have already noticed (121) that the vapour densities of phosphorus and arsenic are anomalous. With respect to the isomorphous relations of the elements of this group we refer the student to the chapter on isomorphism.

"The analogy in composition and properties, manifested by the similar compounds of the five elements, is most striking and complete; although the obvious properties of one set of bodies are sometimes represented by the latent properties of their analogues. The series of corresponding chlorides, oxides, and sulphides is very perfect, as shown below:—

Cl_3N	N_2O	N_2O_4	N_2S_2	P_2S_5
Cl_3P	N_2O_2	Sb_2O_4	As_2S_2	As_2S_5
Cl_3As	N_2O_3	Bi_2O_4	Bi_2S_2	Sb_2S_5
Cl_3Sb	P_2O_3	N_2O_5	P_2S_3	Sb_2S_2O
Cl_3Bi	As_2O_3	P_2O_5	As_2S_3	Bi_2Te_2S"*
Cl_5P	Sb_2O_3	As_2O_5	Sb_2S_3	
Cl_5Sb	Bi_2O_3	Bi_2O_5	Bi_2S_3	

4. *Silicon class.*—Three different atomic weights are assigned to silicon. According to one view, its atomic weight is 21·3, the formula of silicic acid being SiO_3; according to another view its atomic weight is 14, the formula of silicic acid being SiO_2. We have already noticed (171) the reasons which induce some chemists to adopt the latter formula in preference to the first. If we adopt Gerhardt's view, that the molecules of all substances occupy two volumes (see par. 120) in the gaseous state, and if the reasoning which has led chemists to double the old atomic weights of carbon, oxygen, sulphur, &c., be correct, it follows that the atomic weight of silicon must be 28, and the atomic weights of the other members of the group must be increased in like proportion; these new atomic weights we have given in the table of elements. Zirconium is placed by some chemists in this class, and some include boron; but the vapour-densities of some of the compounds of boron would rather indicate that it was

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* Odling's "Manual of Chemistry."

allied to the members of the third group. Professor Miller thus alludes to the *analogies* of the silicon group in the second volume of his "Elements of Chemistry;"—"Silicon presents a certain analogy with boron in its tendency to unite with fluorine and with nitrogen; but its relationship to niobium and tantalum is still more strongly marked, not only in these particulars, but in its tendency to form an acid with two atoms of oxygen, and its production of a volatile liquid bichloride. Silicon likewise exhibits a similar resemblance to titanium and tin. These metals might probably be arranged thus in a series, parallel with niobium and tantalum:*—

Silicon.

Niobium	Titanium
Tantalum	Tin."

271. *Equivalents.*—Although equivalents are the proportions in which bodies can replace one another in combination, they are generally made synonymous, in chemical writings, with combining proportions, or atomic weights, which is incorrect. In order to determine the equivalents of any two bodies, there *must* be some analogy between them; they must fulfil the same functions. If a body, therefore, performs more than one function, it must have more than one equivalent; consequently, *when we speak of the equivalent of a body, we should always indicate to what other body, to what functions, to what properties, that equivalent corresponds.*

272. The following groups of bodies perform the same functions:—1st. The majority of the metals. 2nd. Oxygen, sulphur, selenium, and tellurium. 3rd. Fluorine, chlorine, bromine, iodine, and *manganese.* 4th. The salifiable oxides. 5th. The acids. 6th. The methylic,

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* The student will not have failed to notice, that in this new classification of the elements, that several of the elements formerly classed amongst the metals are now placed with the metalloids. They mark the transition between the two classes of elements. They share with the metals—1, the metallic lustre; 2, conductivity of heat; 3, conductivity for electricity; 4, density. They possess, like the metalloids, the property—1, of being acidifiable; 2, of forming only feeble salifiable bases; 3, of combining easily with the metals, in the manner of an electro-negative body; 4, some of them form a gaseous compound with hydrogen. These characters, of course, are not absolute. Prof. Jerome Nicklès observes, that though they have a metallic lustre, they are all *brittle;* he therefore proposes to consider as *semi-metals* those metallic elements which are neither ductile nor malleable; in other words, the *brittle metals.*

ethylic, and amylic alcohols. 7th. The formic, acetic, and butyric amides. "I admit that we can determine the equivalents of the bodies which compose each of these groups; but that we can never determine the equivalent of a metal in respect to that of an acid; or the equivalent of an oxide in respect to that of an amide. Simple bodies, oxides, acids, salts, alcohols, amides, &c., fulfil entirely different functions; and it is quite impossible to establish an equivalence amongst them."—*Laurent.*

273. Iron must have two different equivalents in its two basic oxides, for in protosalts of iron (ferrous salts), 28 of iron is the equivalent of 1 of hydrogen; in persalts (ferric salts),* $18\frac{2}{3}$ of iron is the equivalent of 1 of hydrogen; in ferric acid it must also have another and different equivalent. In the same way, mercury has two equivalents; in mercurous salts it is 200, in mercuric salts it is 100. Manganese must have four different equivalents in the four compounds, permanganic acid, manganic acid, sesquioxide of manganese, protoxide of manganese. As the permanganates are isomorphous with the perchlorates, 55·2, the quantity of manganese in one atom of permanganic acid, must be the equivalent of 35·5 of chlorine, which is the quantity of that element in one atom of perchloric acid. The manganates are isomorphous with the sulphates: 27·6, the quantity of manganese in one atom of manganic acid, must therefore be the equivalent of 16 of sulphur, the quantity of that element in one atom of sulphuric acid; 18·4 of manganese in manganic salts, and 27·6 in manganous salts, must be the equivalent of 1 of hydrogen. When an element has two or more different equivalents, the different equivalents might be indicated by attaching to the symbol of the element one of the Greek letters, as α for the lowest equivalent number, β for the next, γ for the next, and so on.

274. The equivalents of bodies are, therefore, the relative quantities which replace each other in actual or ideal

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* When a metal forms two classes of salts, as the proto and per-oxides, it has become the fashion of late to indicate the class of salts by attaching to the name of the metal *ous* for the lowest class, and *ic* for the highest; thus, instead of saying protosalts of iron, we say ferr*ous* salts, and, instead of persalts, ferr*ic* salts; and we, in like manner, indicate the equivalent of the metal, where it has more than one equivalent, by calling one the ferrous atom, the other the ferric atom.

substitutions; they may correspond to atoms or to molecules, or they may bear a simple numerical relation to either of these. And the number of equivalents which may be assigned to any body will be equal to the number of chemical functions it fulfils.

275. Mr. Griffin regards a body, which has two or more equivalents, as different in its different equivalents as if it were in each case a distinct and separate body. What we have just now been regarding as different equivalents, he regards as different atomic weights. He says, "I hold the opinion, that when the change in the atomic weight occurs, a change takes place simultaneously in the *quality* of the atom; so that, for example, the mercur*ic* atom is not merely half the weight of the mercur*ous* atom, but is endowed with different chemical properties, and capable of producing compounds which also differ in properties from the compounds of the mercurous atom; so, also, the ferr*ic* atom is not merely two-thirds of the quantity of iron that is contained in the ferrous atom, but is a different chemical agent, possessing properties that are peculiar to itself, and not the same as the properties of the ferr*ous* atom. The characteristics of the ferr*ous* and ferr*ic* atoms do not, on this view, depend upon their relations to other bodies, nor upon the equivalents of other bodies, but are inherent, and not conditional, properties. Each is a single, complete *chemical atom*, and neither of them is an *equivalent* in any other sense." Professor Brodie appears to hold similar views; at least, he considers that the elements in the allotropic state function as distinct elements, with different atomic weights, to what the same elements have in their ordinary states (see par. 198).

276. *Atomic weights.*—A molecule or molecular atom of any element is, as we have before stated, the least quantity of that element which can exist in the free state; an atom or elementary atom of any element is the least quantity which can exist in combination. Three systems of atomic weights have been proposed. One system, and it is the one which has been almost universally adopted in this country, is founded upon the hypothesis of Dalton, that the most stable compound of two elements must be binary, *i. e.*, composed of one atom of each of the elements; now, as the most stable combination of oxygen and hydro-

gen is water, and as the hydrogen and oxygen are united, in this compound, in the proportion of one part of hydrogen to eight parts of oxygen, water has been regarded by Dalton, Davy, Woollaston, Henry, and others, to be, in accordance with the Daltonian canon, a binary compound, and therefore the weight of an atom of oxygen, as compared to that of hydrogen, must be as 8 to 1, and the rational formula for water must be HO. We give, in accordance with this system of atomic weights, the rational formulæ of hydrochloric acid, chloride of sodium, water, and oxide of silver,—

Hydrochloric acid $= HCl$
Chloride of sodium $= NaCl$
Water $= HO$
Oxide of silver $= AgO$

277. Berzelius considered that ***simple substances in the gaseous state contain, under like conditions of temperature and pressure, equal numbers of atoms in equal volumes.*** The formula for water, according to this system, must therefore be H_2O,* because hydrogen and oxygen combine in the proportion of two volumes of the former to one of the latter element, to form water. The atomic weights in this system are the same as those in the former system (276), with the exception of those of HYDROGEN, NITROGEN, PHOSPHORUS, CHLORINE, BROMINE, IODINE, and FLUORINE, which have half the values assigned to them in that system, viz.:—$(O = 8)$; $H = 0{\cdot}5$; $N = 7$; $P = 15{\cdot}5$; $Cl = 17{\cdot}75$; $I = 63{\cdot}18$; $Br = 40{\cdot}0$; $F = 9{\cdot}35$. Metallic oxides are represented by the same formulæ in both systems. The formulæ of hydrochloric acid, chloride of sodium, water, and oxide of silver, in accordance with this system of atomic weights, we here give:—

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* "Berzelius assumed that those bodies which possessed the strongest affinity for oxygen, united with it as in the proportion of 2 atoms to 1; and all his old tables of the atomic constitution of bodies are, in fact, constructed on this principle.

"The reasons he assigns for this inference are curious, reminding one of those of the Indian philosopher for considering that the smallest portion of matter visible to the eye must consist of at least six atoms. He contends that a combination of atom with atom does not exist in nature; because, being composed of two spheres, it would only be extended in a linear direction; whereas, whatever possesses substance is composed of three, four, five, six, or some still larger number of spherical atoms, the sphere constituting, as it were, the germ of those geometrical forms, which the crystals of all bodies exhibit with so much regularity."—*Daubeny on the Atomic Theory.*

Hydrochloric acid = H_2Cl_2 | Water = H_2O
Chloride of sodium = $NaCl_2$ | Oxide of silver = AgO

278. Gerhardt adopted, like Berzelius, the hypothesis that simple substances in the gaseous state contain equal numbers of atoms in equal volumes; but he carried out the system more fully than Berzelius had done. The halving of the equivalents was extended by Gerhardt to the metals. For mercuric oxide contains 8 parts of oxygen to 100 parts of mercury, and the vapour-density of mercury is to that of oxygen nearly as 6·9 : 1·1; hence, for the formation of mercuric oxide, two volumes of vapour of mercury and one volume of oxygen gas are required; for 2 × 6·9 : 1·1 = 100 : 8 (nearly). According to this, the equivalent of mercury (that of oxygen being 8) is equal to 50, and the formula of mercuric oxide is Hg_2O, that of mercurous oxide = Hg_4O. Now, since the chemical relations of mercuric oxide are analogous to those of cupric oxide, ferrous oxide, zinc oxide, manganous oxide, magnesia, lime, potash, &c., it follows that these latter are not composed of CuO, FeO, ZnO, MnO, MgO, CaO, KO, &c., but of Cu_2O, Fe_2O, Zn_2O, Mn_2O, Mg_2O, Ca_2O, K_2O, &c.; their formulæ are thus brought into accordance with that of water, H_2O, and the equivalents of these metals, compared with that of oxygen, are reduced one-half.

279. Gerhardt proposed two sets of formulæ; in the first, he adopted Berzelius's atomic weights for the metalloids, but halved the atomic weights of the metals, for the reasons given above. The formulæ of most bodies corresponded in the first system to four volumes (oxygen = 8); but there were some exceptions to the rule, these were made to correspond by doubling their formulæ; this system is, therefore, called the *four-volume system* of Gerhardt. We here give the formulæ of hydrochloric acid, chloride of sodium, water, and oxide of silver, according to this system:—

Hydrochloric acid = H_2Cl_2 | Water - - = H_2O
Chloride of Sodium = Na_2Cl_2 | Oxide of silver = Ag_2O

280. In the other system proposed by Gerhardt he doubled the atomic weights of O, Se, Te, and C, whilst the atomic weights of the other elements remain as in the first or Daltonian system (276). The atomic weights of

compound bodies he made to correspond to two volumes of vapour (1 of H, or 16 of O = 1 volume), and as the combining quantities of the elements, and some compound radicals, correspond only to one volume of vapour, Gerhardt has proposed to double the atomic weight of the uncombined atom of these bodies so as to make them correspond to two volumes of vapour. (Consult pars. 120, 121, 122). We here give the formulæ of hydrochloric acid, chloride of sodium, water, and oxide of silver, according to this two-volume system of Gerhardt:—

Hydrochloric acid = HCl
Chloride of sodium = $NaCl$
Water - = H_2O
Oxide of silver = Ag_2O

281. *This last system is now beginning to be very generally adopted.*

282. *Arguments for doubling the atomic weight of oxygen, &c.*—We shall now give the arguments for doubling the atomic weights of O, S, Se, Te, and C.

283. 1st.—In all volatile organic compounds, the constitution of which has been accurately determined, the number of atoms of these elements is always even, if we consider the weights of the atoms to be respectively 6, 8, 16, &c. Provided that all such compounds are assumed to correspond to two volumes of vapour ($H = 1$).

284. 2nd.—Purely chemical considerations appear to show that in organic compounds, independently of any assumption as to vapour-volumes, the number of atoms of carbon, oxygen, and sulphur, is always even.

285. 3rd.—When oxygen or sulphur replaces hydrogen in organic compounds, 2 units of weight of hydrogen are replaced by 16 of oxygen or 32 of sulphur; 4 units of hydrogen by 32 of oxygen, and so on: in no case is one unit of weight of hydrogen replaced by 8 of oxygen.

286. 4th.—The least quantity of oxygen or sulphur set free in any re-action is either 32 or 64, or is some multiple of 32 or 64. In like manner, the least quantity of oxygen or sulphur which re-acts with any compound body, is a multiple of 16 or 32 by an even number.

287. 5th.—It is now generally admitted as a law that, in the case of the elements, one molecule consists of two associated atoms; there exists, however, at least one exception to it. The vapour-density of phosphorus, even at a temperature of 1,010° C., corresponds to half a

volume, the atomic weight being taken as 31. Since sulphur, which is less volatile than phosphorus, is a perfect gas, even at 860°, we cannot admit that the case is otherwise with phosphorus, or reasonably suppose that the vapour-density would correspond to one volume if determined at a still higher temperature. We must, therefore, admit that the molecule of phosphorus corresponding to two volumes of vapour contains four atoms, and not two like that of nitrogen; while nothing is more certain than that the atomic weights of phosphorus and nitrogen are respectively 31 and 14. In like manner, the vapour-density of arsenic appears also to correspond to half a volume only, though it has not yet been determined at temperatures very far above the boiling point.*

288. Dr. Odling, who has devoted great attention to this subject, has written a very elaborate paper upon it,† which we shall now give almost completely.

289. Whether an atom of water contains the same quantity, or double the quantity, of hydrogen that is contained in an atom of hydrochloric acid, and whether the atomic weight of oxygen is 8 or 16, are concrete examples of the many disputed questions which lie at the very basis of scientific chemistry. These many primary questions are so intimately connected with one another, that if the answer to nearly any one of them were fully agreed upon, that single unanimity might almost determine an entire unanimity. But to arrive at such a desirable consummation, it is necessary for some one or other of these questions to be fairly argued out upon premises that are admitted by all to be indisputable. And, herein lies the great difficulty, because, in reality, each one of us has formed his opinion upon the single question, rather by its bearings upon all the other disputed questions, than from well-defined premises of any kind. Each party has assumed, instinctively, certain points that are not proven, or are disallowed; and from these assumptions has deduced, in a great measure, his conclusion upon all the questions. Moreover, to no one question can there be given an answer the correctness of which is proveable

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* Dr. Walcott Gibbs, in the *American Journal of Science*, vol. xxxi.

† Dr. Odling, "On the Atomic Weights of Oxygen and Water:" *Quarterly Journal of the Chemical Society*, vol. xi.

to demonstration. Almost every fact may be interpreted in several different ways; and it becomes an argument from probability, from analogy, from simplicity, from consequences, as to which interpretation is most exact. But, apart from the absolute accuracy or falsity of any explanation, it is evidently most inconsequent to interpret, as many chemists do, a certain set of facts in one special manner, and a precisely similar set of facts in an opposite manner. Now, it is to this time-honoured inconsistency that I wish particularly to direct your attention.

290. The elementary bodies unite with one another in certain fixed or definite proportions to form an infinite variety of compound bodies. We find by experiment that one part of hydrogen unites with 35·5 parts of chlorine to form the compound body chloride of hydrogen, and that 35·5 parts of chlorine unite with 23 parts of sodium to form the compound body, chloride of sodium. We take the numbers 1, 35·5, and 23, to represent the combining proportions of hydrogen, chlorine, and sodium, respectively; and, in a similar manner, there have been assigned to other of the elements certain numbers which express, respectively, the least proportion of the element that unites with one part of hydrogen, or that replaces one part of hydrogen to unite with 35·5 parts of chlorine. Thus:—

1 part of hydrogen unites with {
35·5 parts of chlorine,
or 19 parts of fluorine,
or 80 parts of bromine,
or 127 parts of iodine;

and 1 part of hydrogen
or 23 parts of sodium
or 32·5 parts of zinc
or 108 parts of silver
} unite with 35·5 parts of chlorine.

The proportion in which hydrogen enters into a combination, being less than that of any other element, is assumed as unity; and as the quantity of sodium, or zinc, or silver, that displaces 1 part of hydrogen from its combination with 35·5 parts of chlorine, also displaces it from its combination with 19 parts of fluorine, or with 80 parts of bromine, or with 127 parts of iodine, it is evident that the numbers 1, 19, 23, 32·5, 35·5, 80, 108, and 127, indicate generally the proportions in which the elements hydrogen, fluorine, sodium, zinc, chlorine, bromine, silver, and iodine, unite with one another. The above proportional numbers result from a common well-defined relation to the standard of comparison; they are mere results of experiment, uncontrolled by any theory whatever. So far as we have yet gone, our idea of the combining proportion of an element is the least quantity of the element that can unite with, or replace, 1 part of hydrogen. But this simple idea has very speedily to receive an important modification. We find the smallest quantity of nitrogen that can unite with 1 part of hydrogen to be 4·7 parts, but the combining proportion of nitrogen is fixed, not at 4·7 parts, but at three times that quantity, or 14 parts. We find that 1 part of hydrogen unites with 35·5 parts of chlorine to form hydrochloric acid, and that 1 part of hydrogen unites with 4·7 parts of nitrogen to form ammonia. We take 35·5 as the proportional number for chlorine; why do we not take 4·7 as the proportional number for nitrogen? Why do we not express ammonia by the formula HN, precisely as we express hydrochloric acid by the formula HCl? To avoid the confusion that would arise from using the same letter to express two different quantities, we will take the symbol Az to represent 4·7 parts of nitrogen; so that $3\,\mathrm{H\,Az} = \mathrm{H_3N}$. Now the formula $\mathrm{H\,Az}$ is in accordance with all the considerations hitherto presented to our notice; it is more simple than the formula $\mathrm{H_3N}$, and, by its means, ammoniacal compounds in general might be represented as analogous to chlorine and fluorine compounds; thus,—

Ammonia	HAz	HCl
Trizincamide	ZnAz	ZnCl
Trimercuramide	HgAz	HgCl
Potassamide	$\mathrm{KAz, 2HAz}$	$\mathrm{KCl, 2\,HgCl}$
Sal-ammoniac	$\mathrm{HCl, 3HAz}$	$\mathrm{KI, 3\,HgCl}$.

Why, then, have chemists unanimously rejected the formula HAz, and adopted the formula $\mathrm{H_3N}$? Now, although this last formula may have originated in part from accident, and have been retained in part from habit, yet we have no lack of real arguments to show the necessity, or at any rate advisability, of maintaining it. I believe the principal arguments are the following:—

1. Because it is found that a given bulk of gaseous

ammonia contains three times as much hydrogen as the same bulk of hydrochloric acid.

2. Because it is found that a given bulk of nitrogen combines with three times as much hydrogen as does the same bulk of chlorine; and that the relative weights of equal bulks of nitrogen and chlorine and hydrogen are as 14 : 35·5 : 1.

3. Because certain undoubted analogies and ratios of nitrogenized bodies are concealed by formulæ in which $Az = 4{\cdot}7$, and are manifested by formulæ in which $N = 14$.

4. Because, in ninety-nine cases out of a hundred, the quantity of ammonia which is the agent or resultant of a reaction must contain three units of hydrogen, or some multiple of three units of hydrogen; and consequently fourteen, or some multiple of fourteen, parts of nitrogen.

5. Because, in the majority of the compounds which ammonia forms with other bodies, the ammonia must be represented with three units, or some multiple of three units, of hydrogen.

6. Because, although the composition of some few nitrogenized bodies may be represented most simply by formulæ in which $Az = 4{\cdot}7$, yet the great majority are represented most simply by formulæ in which $N = 14$.

7. Because, in ammonia, the actual or potential replacement of hydrogen takes place definitely in thirds, by three successive stages.

291. Although the above arguments cannot be considered to prove absolutely to demonstration that the atom of nitrogen, or the smallest indivisible quantity of nitrogen, that can enter into a combination, is really fourteen times as great as the atom of hydrogen, yet they present so great a sum of probabilities in favour of that conclusion, that chemists have been unanimous in accepting it. With one exception, all these arguments apply with equal force to the elements phosphorus, arsenic, antimony, and bismuth; and we consequently find that all chemists have agreed to accept, for the respective atomic weights of these bodies, three times the smallest quantity of the body which unites with 1 part of hydrogen, or with 35·5 parts of chlorine. The excepted argument is that relating to the vapour-densities of the elements in question. But, in default of this argument, we can bring forward another of a most cogent nature in behalf of the

triplication of the atomic weights of phosphorus, arsenic, antimony, and bismuth, namely, that derived from their gradational analogies to nitrogen. If the atomic weight of nitrogen is 14, and not 4·7, the atomic weights of phosphorus, arsenic, antimony, and bismuth, must be respectively 31, 75, 120, and 213, and not the thirds of these numbers.

292. From the above considerations concerning nitrogen and its congeners, in which all chemists are agreed, it appears that while the determination of the smallest proportion of an element that can unite with or replace one part of hydrogen is a question purely experimental, the determination of the atomic weight of an element is a question for the judgment, and one that can only be decided by an intimate knowledge and due consideration of very many circumstances connected with the body. Now, although the judgment of chemists has been unanimous with respect to nitrogen and its congeners, such unanimity has not prevailed in reference to many other elements. Thus, with regard to silicon,—

Thomson represented chloride of silicon by the formula—

$SiCl$, where the atomic weight of silicon $= 7·12$;

Gmelin, by the formula—

$SiCl_2$, where the atomic weight of silicon $= 14·25$;

Berzelius, by the formula—

$SiCl_3$, where the atomic weight of silicon $= 21·37$;

whereas, in my opinion, the balance of argument is in favour of the formula—

$SiCl_4$, where the atomic weight of silicon $= 28·50$.

293. In reference to a body of such doubtful analogies as silicon—whose combinations, moreover, are remarkable for their complexity—it is natural that differences of opinion with regard to its atomic weight should be entertained by different chemists, according to their particular modes of viewing the subject; and not only with regard to silicon, but to boron, to gold, to uranium, to tantalum, and indeed to all elements the analogies of which have not been well established. But in reference to such well-known elements as oxygen, sulphur, and carbon, there

certainly ought to be the same unanimity that obtains in the case of nitrogen; though in reality we find the discord even more violent than in the case of silicon.

294. We will now proceed to investigate, from undisputed data, the atomic weight of oxygen, and the atomic weight of water. Is the atom of water $HO = 9$, or $H_2\Theta = 18$?

295. All chemists admit—firstly, that the atom of chlorhydric acid consists of 1 part of hydrogen, united with 35·5 parts of chlorine: secondly, that the atom of ammonia consists of 3 parts of hydrogen united with 14 parts of nitrogen; and that, as compared with 35·5 parts of chlorine, 14 parts of nitrogen is the smallest quantity of nitrogen that can enter into a combination. Now I wish to show—firstly, that if the atom of chlorhydric acid consists of 1 part of hydrogen united with 35·5 parts of chlorine, and if the atom of ammonia consists of 3 parts of hydrogen united with 14 parts of nitrogen, then the atom of water must consist of 2 parts of hydrogen united with 16 parts of oxygen: secondly, that if 35·5 parts of chlorine constitute the smallest indivisible quantity of chlorine that can enter into a combination, and if 14 parts of nitrogen constitute the smallest indivisible quantity of nitrogen that can enter into a combination, then 16 parts of oxygen constitute the smallest indivisible quantity of oxygen that can enter into a combination; or, in other words, that the atomic weight of oxygen is 16, when compared with the atomic weight of hydrogen as 1, of chlorine as 35·5, and of nitrogen as 14. Every argument that induces us to accord to the atom of nitrogen the number 14, rather than the number 4·7, should also induce us to accord to the atom of oxygen the number 16, rather than the number 8.

296. I propose to review, briefly, all the arguments we have admitted in the case of nitrogen, and to prove that they are equally applicable in the case of oxygen; or to show why it is that ammonia must be written H_3N, and water $H_2\Theta$, as compared with hydrochloric acid, HCl.

NITROGEN.	OXYGEN.
a. Because it is found that a given bulk of gaseous ammonia contains three times	*a. Because it is found that a given bulk of gaseous water contains twice as much*

as much hydrogen as the same bulk of hydrochloric acid.

β. Because it is found that a given bulk of nitrogen combines with three times as much hydrogen as does the same bulk of chlorine; and that the relative weight of equal bulks of nitrogen and of chlorine are as 14 *to* 35·5.

hydrogen as the same bulk of hydrochloric acid.

β. Because it is found that a given bulk of oxygen combines with twice as much hydrogen as does the same bulk of chlorine; and that the relative weights of equal bulks of oxygen and of chlorine are as 16 *to* 35·5.

297. I attach very great importance to these first two arguments, which apply with equal force to the duplication of oxygen and the triplication of nitrogen; to the binhydric character of water, and the terhydric character of ammonia.

γ. Because certain undoubted analogies and ratios of nitrogenized bodies are concealed by formulæ in which $Az = 4·7$, *and are manifested by formulæ in which* $N = 14$.

γ. Because certain undoubted analogies and ratios of oxydized bodies are concealed by formulæ in which $O = 8$, *and are manifested by formulæ in which* $\Theta = 16$.

298. These reasons apply with about equal force, though in a somewhat different manner, to nitrogen and to oxygen respectively. Thus with $Az = 4·7$ the analogies of nitrogen and chlorine compounds would be concealed by the formulæ, for we should have,—

Nitrous acid.		Chlorous acid.
$H\,Az_3\Theta_2$	instead of $H\,N\Theta_2$ analogous to	$H\,Cl\,\Theta_2$.

Nitric acid.		Chloric acid.
$H\,Az_3\Theta_3$	instead of $H\,N\Theta_3$ analogous to	$H\,Cl\Theta_3$.

Pernitric oxide.		Perchloric oxide.
$Az_6\Theta_4$	instead of $N_2\Theta_4$ analogous to	$Cl_2\Theta_4$.

299. With $O = 8$, the relation of water to the alcohols as the undoubted vanishing point of the series, would not be manifested, as it is in the formulæ with $\Theta = 16$. Thus, if we write alcohol $C_4H_6O_2$, wood spirit $C_2H_4O_2$, and water $H\,O$, the relation of water to the alcohols does not appear; but in the following series of formulæ it is perfectly apparent:—

$\text{₵}_5 H_{12} \Theta$ amylic alcohol
$\text{₵}_4 H_{10} \Theta$ butylic „
$\text{₵}_3 H_8 \Theta$ propylic „
$\text{₵}_2 H_6 \Theta$ ethylic „
$\text{₵} H_4 \Theta$ methylic „
$H_2 \Theta$ hydric „

300. The relation of water to the alcohols, as shown in the above formulæ, is not a mere paper relation, but has its foundation in experiment. When alcohol and water respectively are acted upon by potassium, by chloride of benzoyl, by pentachloride of phosphorus, and by a host of other reagents, the reactions are acknowledged by all to be precisely parallel. All chemists, no matter what formulæ they employ, recognise the fact that the quantity of water which, in a reaction, corresponds to one proportion of alcohol, must contain two units of hydrogen.

201. Similarly, with regard to the hydrated bases and acids. If we write hydrate of potass $K\,H\,O_2$; hydrated hypochlorous acid $H\,Cl\,O_2$; and water $H\,O$, the relation of the formulæ, as representing comparable quantities, does not appear. But in the following series it is perfectly evident:—

$K\,K\,\Theta$ potass oxide
$K\,H\,\Theta$ potass hydrate
$H\,H\,\Theta$ water
$H\,Cl\,\Theta$ hypochlorous acid
$K\,Cl\,\Theta$ potass hypochlorite
$Cl\,Cl\,\Theta$ hypochlorous anhydride.

302. The following reactions, among many others, show that the quantity of water which corresponds to one proportion of hydrate of potass, or of hypochlorous acid, must contain two units of hydrogen:—

1. *Action of chloride of benzoyl.**

$$K H \Theta + \text{₵}_7 H_5 Cl \Theta = K Cl + \text{₵}_7 H_6 \Theta_2$$
$$H_2 \Theta + \text{₵}_7 H_5 Cl \Theta = H Cl + \text{₵}_7 H_6 \Theta_2$$

2. *Action of chlorine.*

$$K H \Theta + Cl_2 = H Cl \Theta + K Cl$$
$$H_2 \Theta + Cl_2 = H Cl \Theta + H Cl.$$

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* The student may pass over the examples selected from organic chemistry until he has studied Chapters VII., VIII., IX., and X., he ought then to return to this chapter and re-study it.

δ. Because, in ninety-nine cases out of a hundred, the quantity of ammonia which is the agent or resultant of a reaction, must contain H_3, *or some multiple of* H_3; *and, consequently,* 14, *or some multiple of* 14 *parts of nitrogen.*

δ. Because, in ninety-nine cases out of a hundred, the quantity of water which is the agent or resultant of a reaction, must contain H_2, *or some multiple of* H_2; *and, consequently,* 16, *or some multiple of* 16 *parts of oxygen.*

303. This argument is one of the most cogent that can be adduced. It is well illustrated in the case of nitrogenized, but infinitely better in the case of oxidized compounds. Let us adduce some nitrogenous reactions.

1. *Formation of ammonia from sal ammoniac.*

$$NH_4Cl + CaH\Theta = NH_3 + CaCl + H_2\Theta; \text{ or}$$
$$Az_2H_4Cl + CaHO_2 = Az_2H_3 + CaCl + H_2O_2.$$

2. *Formation of ammonia from nitrate of potass.*

$$KN\Theta_3 + 8H = KH\Theta + NH_3 + 2H_2\Theta; \text{ or}$$
$$KAz_2O_6 + 8H = KHO_2 + Az_2H_3 + 4HO.$$

3. *Formation of cyanogen from oxalate of ammonia.*

$$2NH_3.\text{Ꞓ}_2H_2\Theta_4 - 4H_2\Theta = 2\text{Ꞓ}N; \text{ or}$$
$$2Az_2H_3.C_4H_2O_8 - 8HO = 2C_2Az_2; \text{ or}$$
$$Az_2H_3, C_2HO_4 - 4HO = C_2Az_2.$$

4. *Formation of benzamide.*

$$NH_3 + \text{Ꞓ}_2H_5(\text{Ꞓ}_7H_5\Theta)\Theta = NH_2(\text{Ꞓ}_7H_5\Theta) + \text{Ꞓ}_2H_6\Theta; \text{ or}$$
$$Az_2H_3 + C_4H_5(C_{14}H_5O_2)O_2 = Az_2H_2(C_{14}H_5O_2) + C_4H_6O_2.$$

304. Express the above reactions howsoever you please, you cannot represent any one of them with a proportion of ammonia containing less than three units of hydrogen, nor, consequently, with less than 14 parts of nitrogen. And, whenever more than three units of hydrogen are required, you must take some multiple of three units of hydrogen, and some multiple of 14 parts of nitrogen; and ninety-nine cases out of a hundred will yield the same result. As an example of those cases in which it is possible to represent the acting or resulting proportion of ammonia

with less than three units of hydrogen, I may adduce the—

5. *Formation of triethylamine.*

$\mathrm{N\,H_3 + 3\,Ȼ_2\,H_5\,I = N{\cdot}3\,Ȼ_2\,H_5 + 3\,H\,I}$; or
$\mathrm{Az_3\,H_3 + 3\,C_4\,H_5\,I = 3\,Az\,C_4\,H_5 + 3\,H\,I}$; or
$\mathrm{Az\,H + C_4\,H_5\,I = Az\,C_4\,H_5 + H\,I}$.

305. And similarly with trimercuramine, $\mathrm{N\,Hg_3} = 3\,\mathrm{Az\,Hg}$; though no one really thinks of writing the formulæ of these bodies with only one unit of ethyl or of mercury respectively.

306. Let us now revert to oxygenous reactions. I wish to show that, in ninety-nine cases out of a hundred, when water appears as the agent or resultant of a reaction, it is impossible to represent that water with less than two atoms of hydrogen.

1st. Whenever an alcohol, ketone, or other oxidized organic compound yields a hydrocarbon by dehydration, the water eliminated contains two, or some multiple of two, units of hydrogen.

1. *Formation of olefiant gas from alcohol.*

$\mathrm{Ȼ_2\,H_6\,\Theta - H_2\,\Theta = Ȼ_2\,H_4}$; or
$\mathrm{C_4\,H_6\,O_2 - 2\,HO = C_4\,H_4}$.

2. *Formation of mesitylene from acetone.*

$\mathrm{3\,Ȼ_3\,H_6\,\Theta - 3\,H_2\,\Theta = Ȼ_9\,H_{12}}$; or
$\mathrm{3\,C_6\,H_6\,O_2 - 6\,HO = C_{18}\,H_{12}}$.

3. *Formation of cymene from camphor.*

$\mathrm{Ȼ_{10}\,H_{16}\,\Theta - H_2\,\Theta = Ȼ_{10}\,H_{14}}$; or
$\mathrm{C_{20}\,H_{16}\,O_2 - 2\,HO = C_2\,H_{14}}$.

Other compounds than hydrocarbons result from similar equations; thus,—

4. *Formation of acrolein from glycerin.*

$\mathrm{Ȼ_3\,H_8\,\Theta_3 - 2\,H_2\,\Theta = Ȼ_3\,H_4\,\Theta}$; or
$\mathrm{C_6\,H_8\,O_6 - 4\,HO = C_6\,H_4\,O_2}$.

2nd. Whenever an organic acid yields a pyroacid, or other pyrogenous product, by dehydration.

1. *Formation of carbonic oxide from formic acid.*

$\mathrm{Ȼ\,H_2\,\Theta_2 - H_2\,\Theta = Ȼ\,\Theta}$; or
$\mathrm{C_2\,H_2\,\Theta_4 - 2\,HO = C_2\,O_2}$.

2. *Formation of maleic from malic acid.*

$\text{Ȼ}_4 H_6 \text{Ɵ}_5 - H_2 \text{Ɵ} = \text{Ȼ}_4 H_4 \text{Ɵ}_4$; or
$C_8 H_6 O_{10} - 2\, HO = C_8 H_4 O_8$.

3. *Formation of pyruvic from tartaric acid.*

$\text{Ȼ}_4 H_6 \text{Ɵ}_6 - H_2 \text{Ɵ} - \text{Ȼ} \text{Ɵ}_2 = \text{Ȼ}_3 H_4 \text{Ɵ}_3$; or
$C_8 H_6 O_{12} - 2\, HO - 2\, C O_2 = C_6 H_4 O_6$.

4. *Formation of aconitic from citric acid.*

$\text{Ȼ}_6 H_8 \text{Ɵ}_7 - H_2 \text{Ɵ} = \text{Ȼ}_6 H_6 \text{Ɵ}_6$; or
$C_{12} H_8 O_{14} - 2\, HO = C_{12} H_6 O_{12}$.

5. *Formation of pyromucic from mucic acid.*

$\text{Ȼ}_6 H_{10} \text{Ɵ}_8 - 3\, H_2 \text{Ɵ} - \text{Ȼ} \text{Ɵ}_2 = \text{Ȼ}_5 H_4 \text{Ɵ}_3$; or
$C_{12} H_{10} O_{16} - 6\, HO - 2\, C O_2 = C_{10} H_4 O_6$.

3rd. Whenever two compounds act upon one another to form a new compound, with simultaneous elimination of water.

ACTION OF AN ACID UPON A HYDROCARBON.

1. *Sulphobenzide.*

$H_2 S \text{Ɵ}_4 + 2\, \text{Ȼ}_6 H_6 - 2\, H_2 \text{Ɵ} = \text{Ȼ}_{12} H_{10} S \text{Ɵ}_2$; or
$H_2 S_2 O_8 + 2\, C_{12} H_6 - 4\, H O = C_{24} H_{10} S_2 O_4$; or
$H S O_4 + C_{12} H_6 - 2\, HO = C_{12} H_{10} S O_2$.

2. *Sulphobenzidic acid.*

$H_2 S \text{Ɵ}_4 + \text{Ȼ}_6 H_6 - H_2 \text{Ɵ} = \text{Ȼ}_6 H_6 S \text{Ɵ}_3$; or
$H_2 S_2 O_8 + C_{12} H - 2\, HO = C_{12} H\, S_2 O_6$.

3. *Nitro-naphthaline.*

$H N \text{Ɵ}_3 + \text{Ȼ}_{10} H_8 - H_2 \text{Ɵ} = \text{Ȼ}_{10} H_7 (N \text{Ɵ}_2)$; or
$H N O_6 + C_{20} H_8 - 2\, H O = C_{20} H_7 (N O_4)$.

ACTION OF AN ACID UPON AN ALCOHOL.

4. *Phosphovinic acid.*

$H_3 P \text{Ɵ}_4 + \text{Ȼ}_2 H_6 \text{Ɵ} - H_2 \text{Ɵ} = H_2 (\text{Ȼ}_2 H_5) P \text{Ɵ}_4$; or
$H_3 P O_8 + C_4 H_6 O_2 - 2\, HO = H_2 (C_4 H_5) P O_8$.

5. *Benzoic ether.*

$\text{Ȼ}_7 H_6 \text{Ɵ}_2 + \text{Ȼ}_2 H_6 \text{Ɵ} - H_2 \text{Ɵ} = \text{Ȼ}_2 H_5, \text{Ȼ}_7 H_5 \text{Ɵ}_2$; or
$C_{14} H_6 O_4 + C_4 H_6 O_2 - 2\, HO = C_4 H_5, C_{14} H_5 O_4$.

ACTION OF AN ACID UPON AN ALKALI.

6. *Sulph-anilic acid.*

$\mathrm{H_2S\Theta_4 + \text{Ȼ}_6H_7N - H_2\Theta = \text{Ȼ}_6H_7NS\Theta_3}$; or
$\mathrm{H_2S_2O_8 + C_{12}H_7N - 2HO = C_{12}H_7NS_2O_6}$.

7. *Nitraniline.*

$\mathrm{HN\Theta_3 + \text{Ȼ}_6H_7N - H_2\Theta = \text{Ȼ}_6H_6(N\Theta_2)N}$; or
$\mathrm{HNO_6 + C_{12}H_7N - 2HO = C_{12}H_6(NO_4)N}$.

ACTION OF AN ACID UPON AN ACID.

8. *Nitro-salicylic acid.*

$\mathrm{HN\Theta_3 + \text{Ȼ}_7H_6\Theta_3 - H_2\Theta = \text{Ȼ}_7H_5(N\Theta_2)\Theta_3}$; or
$\mathrm{HNO_6 + C_{14}H_6O_6 - 2HO = C_{14}H_5(NO_4)O_6}$.

ACTION OF AN ACID UPON AN ALDEHYD.

9. *Nitro-benzoic aldehyd.*

$\mathrm{HN\Theta_3 + \text{Ȼ}_7H_6\Theta - H_2\Theta = \text{Ȼ}_7H_5(N\Theta_2)\Theta}$; or
$\mathrm{HNO_6 + C_{14}H_6O_2 - 2HO = C_{14}H_5(NO_4)O_2}$.

ACTION OF AN ALKALI UPON AN ALDEHYD.

10. *Hydrobenzamide.*

$\mathrm{2NH_3 + 3\text{Ȼ}_7H_6\Theta - 3H_2\Theta = \text{Ȼ}_{21}H_{18}N_2}$; or
$\mathrm{2NH_3 + 3C_{14}H_6O_2 - 6HO = C_{42}H_{18}N_2}$.

4th. Whenever a salt of ammonia, aniline, or other volatile alkali loses water.

1. *Formation of cyanhydric acid.*

$\mathrm{NH_3, \text{Ȼ}H_2\Theta_2 - 2H_2\Theta = \text{Ȼ}NH}$; or
$\mathrm{NH_3, C_2H_2O_4 - 4HO = C_2NH}$.

2. *Formation of benzanilide.*

$\mathrm{\text{Ȼ}_6H_7N, \text{Ȼ}_7H_6\Theta_2 - H_2\Theta = \text{Ȼ}_6H_6(\text{Ȼ}_7H_5\Theta)N}$; or
$\mathrm{C_{12}H_7N, C_{14}H_6O_4 - 2HO = C_{12}H_6(C_{14}H_5O_2)N}$.

3. *Formation of aceto-nitrile.*

$\mathrm{NH_3, \text{Ȼ}_2H_4\Theta_2 - 2H_2\Theta = \text{Ȼ}_2H_3N}$; or
$\mathrm{NH_3, C_4H_4O_4 - 4HO = C_4H_3N}$.

307. In all the illustrations hitherto brought forward, the water has been the resultant of the reaction. Many of these reactions are capable of being reversed, and the water then appears as the agent of the reaction.

308. But we can also adduce an abundance of other and

most varied instances in which water is the agent of a reaction.

309. The circumstance that $2\,H\,O$ are invariably associated, is strongly suggestive of their being inseparably associated—of their constituting, in fact, but one atom.

ε. *Because, in the majority of the compounds which ammonia forms with other bodies, the ammonia must be represented with three units, or some multiple of three units, of hydrogen.*

ζ. *Because, although the formulæ of some few nitrogenized bodies may be represented most simply by formulæ in which* $Az = 4{\cdot}7$, *yet the great majority are represented most simply by formulæ in which* $N = 14$.

ε. *Because, in the majority of the compounds which water forms with other bodies, the water must be represented with two units, or some multiple of two units, of hydrogen.*

ζ. *Because, although the formulæ of some few oxydized bodies may be represented most simply by formulæ in which* $O = 8$, *yet the great majority are represented most simply by formulæ in which* $\Theta = 16$.

310. This argument applies strongly in the case of nitrogenized, but much more strongly in the case of oxydized compounds.

311. Ammonia, and all derivations of ammonia, in which the whole of the hydrogen is replaced by one single kind of metal, or hydrocarbon, or haloid, might be represented more simply by formulæ in which $Az = 4{\cdot}7$, than by formulæ in which $N = 14$. Thus, triethylamine is written most simply $Az\,\text{Є}_2\,H_5$, though most correctly by $N\,3\,\text{Є}_2\,H_5$.

312. I believe that all other nitrogenized bodies are necessarily represented most simply by formulæ in which $N = 14$.

313. With regard to oxygen, all hydrated oxides, double oxides, hydrated acids, oxy-salts, aldehyds, ketones, alcohols, pseudo-saline ethers, and various other descriptions of compounds, doubtless forming together 99 per cent. of all known compounds of oxygen, cannot be represented so simply by formulæ in which $O = 8$ as by formulæ in which $\Theta = 16$.

314. I have contended, that if the comparable atoms of nitrogenized bodies were correctly formulated, they would

all of them be represented more simply by formulæ in which $N = 14$ than by formulæ in which $Az = 4{\cdot}7$; and I now contend, that if the comparable atoms of oxydized bodies were correctly formulated, they would all be represented more simply by formulæ in which $\Theta = 16$, than by formulæ in which $O = 8$. But precisely as there are some few nitrogenized bodies, which, with the symbol $Az = 4{\cdot}7$, may be divided into thirds, and can thus receive simpler formulæ than with the symbol $N = 14$, so are there some comparatively few oxydized bodies which, with the symbol $O = 8$, may be divided into halves, and can thus receive simpler formulæ than with the symbol $\Theta = 16$. These bodies are the following:—

315. 1st.—Most compounds in which oxygen is united with one kind of matter only, including nearly all the simple metallic oxides.

316. Thus with $\Theta = 16$, water and lime must be written respectively, $H_2\Theta$ and $Ca_2\Theta$, analogous to hydrate of lime, $Ca\,H\,\Theta$; but with $O = 8$ they may be written thus —$H_2\,O_2$ and $Ca_2\,O_2$, analogous to hydrate of lime, $Ca\,H\,O_2$; or thus—$H\,O$ and $Ca\,O$. I do not propose to argue the point whether $Ca\,O$, or $Ca_2\,O_2$ ($= Ca_2\Theta$), is the correct expression for a metallic oxide, lime, any more than I have argued the point whether $Hg\,Az$, or $Hg_3\,Az_3$ ($= Hg_3\,N$), is the correct expression for a metallic nitride, mercuramine. We are at present discussing whether the formula of water is $H\,O$, or $H_2\,O_2$ ($= H_2\Theta$), and the decision upon this point will determine that of the metallic and other simple oxides. It may be observed, however, that many strictly comparable reactions can be effected by means of lime, hydrate of lime, and water respectively, and that in these cases we always require $2\,H\,O$, or $2\,Ca\,O$, to effect the reaction. Of course, if $Ca_2\,O_2$ is the correct expression for the atom of lime, the formula with $\Theta = 16$ is simpler than that with $O = 8$, and similarly with other homogeneous oxides.

317. 2nd.—Bodies analogous to ordinary ether and the homogeneous anhydrides. With $\Theta = 16$, ether and benzoic anhydride must be written respectively,—

$Et_2\Theta$ analogous to $H\,Et\,\Theta$ and $Me\,Et\,\Theta$
Ether. Alcohol. Methyl-ethyl-ether.

And $Bz_2\Theta$, analogous to $H\,Bz\,\Theta$ and $Ot\,Bz\,\Theta$.
Benz-anhydride. Benzoic acid. Othyl-benz-anhydride.

But with $O = 8$ they may be written thus:—

$Et_2 O_2$ analogous to $H\,Et\,O_2$ and $Me\,Et\,O_2$;

And $Bz_2 O_2$ analogous to $H\,Bz\,O_2$ and $Ot\,Bz\,O_2$.

Or thus:—$Et\,O$ and $Bz\,O$.

318. Now all arguments founded on mode of formation, on reactions, on vapour-densities, or seriated position and properties, &c., tend to show that $Et\,O$ and $Bz\,O$ are not correct expressions of the nature of the bodies represented; and if $Et_2 O_2$ and $Bz_2 O_2$ are the correct expressions, it is at once evident that in these cases formulæ with $\Theta = 16$ are simpler than formulæ with $O = 8$.

319. 3rd.—Certain acids, and their salts of one metal, heretofore usually considered monobasic, but which in reality are bibasic. Thus with $\Theta = 16$ the hydrated carbonic, sulphurous, and sulphuric acids, must be represented respectively by the formulæ,—

$H_2\text{Ȼ}\Theta_3$ $\qquad$ $H_2S\Theta_3$ $\qquad$ $H_2S\Theta_4$.

But with $O = 8$ they may be represented thus:—

$H_2C_2O_6$ $\qquad$ $H_2S_2O_6$ $\qquad$ $H_2S_2O_8$.

Or thus, $H\,C\,O_3$ $\qquad$ $H\,S\,O_3$ $\qquad$ $H\,S\,O_4$.

But, in these cases, we can adduce strong evidence to show that the simple formulæ $H\,C\,O_3$, $H\,S\,O_3$, and $H\,S\,O_4$, are not correct expressions of the nature of the bodies; and if the correct expressions are $H_2C_2O_6$, $H_2S_2O_6$, and $H_2S_2O_8$, that is to say, if the acids are bibasic, then the formulæ with $\Theta = 16$ are evidently more simple than those with $O = 8$.

η. Because, in ammonia, the actual or potential replacement of hydrogen takes place definitely in thirds, by three successive stages.	*η. Because, in water, the actual or potential replacement of hydrogen takes place definitely in halves, by two successive stages.*

320. We have no definite nitride that can be represented as ammonia, in which one-half the hydrogen is replaced, as we might expect if the atomic weight of nitrogen was 4·7. We have no definite oxide that can be represented as water, in which one-third the hydrogen is replaced, as we might expect if the atomic weight of oxygen were 8. Thus,—

Chloride.	Oxide.	Nitride.
KCl	KO	HAz
$KCl, HgCl$	KO, HO	Wanting
$KCl, 2\,HgCl$	Wanting	$HAz, 2\,PtAz$.

If we write water $\left.\begin{matrix}H\\H\end{matrix}\right\}\Theta$, and ammonia $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$, we at once see the necessity or reason for the vacancies. In water we can replace a half, but not a third. In ammonia we can replace one-third or two-thirds, but not a half; whereas in marsh gas, $\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}\text{Ȼ}$, we can replace one-fourth, two-fourths, or three-fourths, but not one-third or two-thirds of the hydrogen. We are acquainted with many ammonias in which one, two, and three thirds of the hydrogen are replaced. Such, for instance, as

$N\,H_2\,K$ potassamide
$N\,H\,I_2$ biniodamide
$N\,Hg_3$ trimercuramine.

But the most striking illustration of replacement by thirds is afforded by Hoffmann's researches on the volatile alkaloids, in which he successively replaced one, two, and three atoms of hydrogen by a mere combination of one and the same process.

Ammonia.	Ethylia.	Diethylia.	Ethyl-methyl-aniline.
$N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.$	$N\left\{\begin{matrix}H\\H\\Et\end{matrix}\right.$	$N\left\{\begin{matrix}H\\Et\\Et\end{matrix}\right.$	$N\left\{\begin{matrix}Ph\\Et\\Me\end{matrix}\right.$

321. We are acquainted with many oxides that may be considered as derivatives of water, in which one-half the hydrogen is replaced, or in which both halves are replaced by different elements or groupings. Thus,—

Water.	Alcohol.	Ether.	Methyl-ether.	Phenyl-ether.	Ethylate of potass.
$\Theta\left\{\begin{matrix}H\\H\end{matrix}\right.$	$\Theta\left\{\begin{matrix}H\\Et\end{matrix}\right.$	$\Theta\left\{\begin{matrix}Et\\Et\end{matrix}\right.$	$\Theta\left\{\begin{matrix}Et\\Me\end{matrix}\right.$	$\Theta\left\{\begin{matrix}Et\\Ph\end{matrix}\right.$	$\Theta\left\{\begin{matrix}Et\\K\end{matrix}\right.$

Hydrate of potass.	Oxide of potass.	Zinc oxide of potass.	Hypochlorite of potass.	Hypochlorous acid.	Hypochlorous anhydride.
$\Theta\left\{\begin{matrix}H\\K\end{matrix}\right.$	$\Theta\left\{\begin{matrix}K\\K\end{matrix}\right.$	$\Theta\left\{\begin{matrix}Zn\\K\end{matrix}\right.$	$\Theta\left\{\begin{matrix}K\\Cl\end{matrix}\right.$	$\Theta\left\{\begin{matrix}H\\Cl\end{matrix}\right.$	$\Theta\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$

322. In many cases we can effect the total replacement by the same element or grouping at two successive stages. Thus,—

	$\Theta \left\{ \begin{matrix} H \\ H \end{matrix} \right\}$	Water.
Water and potassium yield	$\Theta \left\{ \begin{matrix} H \\ K \end{matrix} \right\}$	Hydrate of potass.
Hydrate of potass and iodide of ethyl yield -	$\Theta \left\{ \begin{matrix} H \\ Et \end{matrix} \right\}$	Alcohol.
Alcohol and potassium yield - - - -	$\Theta \left\{ \begin{matrix} K \\ Et \end{matrix} \right\}$	Ethylate of potass.
Ethylate of potass and iodide of ethyl yield -	$\Theta \left\{ \begin{matrix} Et \\ Et \end{matrix} \right\}$	Ether.
Ethylate of potass and iodide of methyl yield	$\Theta \left\{ \begin{matrix} Et \\ Me \end{matrix} \right\}$	Methylate of ethyl.
Hydrate of potass and potassium yield - -	$\Theta \left\{ \begin{matrix} K \\ K \end{matrix} \right\}$	Oxide of potass.

323. This brings to a conclusion my arguments upon the atomic weights of oxygen and water, founded on a comparison of the arguments which apply in the case of nitrogen and ammonia. The point that I urge is not so much the absolute point, namely, that the atomic weight of oxygen must be 16, as the relative point, namely, that if the atomic weight of nitrogen is 14 and not 4·7, the atomic weight of oxygen must be 16 and not 8. Every argument that applies to the first case, applies with equal if not greater force to the second. I know very well that some of the arguments I have adduced, as that from analogy, for instance, may be apparently subverted by the subterfuge of writing water $H_2 O_2$; but I also know, that chemists who make use of the formula $H_2 O_2$ to represent water, act most inconsistently if they do not also make use of the formula $H_3 Az_3$ to represent ammonia. There are three consequent methods of formulating chlorhydric acid, water, and ammonia, in respect to one another, namely,—

I.	II.	III.
$H\,Cl$	$H\,Cl$	$H\,Cl$
$H\,O$	$H_2\,O_2$	$H_2\,\Theta$
$H\,Az$	$H_3\,Az_3$	$H_3\,N$

324. The first method was that employed by Dalton, who wrote ammonia O ⦶ = 1 + 5, and water O ⊙ = 1 + 7.

325. But both the following modes are most inconsequent, and therefore reprehensible—

IV.	V.
$HCl = 2$ vol.	$HCl = 2$ vol.
$HO = 1$ vol.	$H_2O_2 = 2$ vol.
$H_3N = 2$ vol.	$H_3N = 2$ vol.

326. Series IV. represents irrelative quantities, and Series V. accords irrelative formulæ to comparable quantities. I would observe, in reference to Series I., II., and III., that the selection of one or other of them involves both a question of fact and a question of convenience. Whether the first or second series really represents comparable quantities—that is to say, whether the atom of water, or the smallest proportion of water that is the agent or resultant of a reaction, contains twice as much hydrogen as the atom, or smallest reacting and resulting proportion of hydrochloric acid, is a question of fact. Whether the formula in the second, or that in the third series, is the most appropriate mode of expressing the fact, may be, to some extent at least, a question of convenience, though, at the same time, it is one of very considerable importance. The same remarks apply to the formulæ for ammonia.

327. But we have an additional argument in favour of the duplication of the atom of oxygen, derived from the series into which it enters. Thus, in all compounds of oxygen with two other kinds of matter, as particularly instanced by ox-acids, and oxy-salts, the oxygen increases by 16 parts; and in none of these compounds can we add, subtract, or replace a less quantity than 16 parts of oxygen. Why this should be, unless the 16 parts constitute an indivisible proportion, or chemical atom, I am at a loss to conceive. The following are illustrations:—

Chlorhydric acid	HCl	or HCl
Hypochlorous acid	$HCl\Theta$	or $HClO_2$
Chlorous acid	$HCl\Theta_2$	or $HClO_4$
Chloric acid	$HCl\Theta_3$	or $HClO_6$
Perchloric acid	$HCl\Theta_4$	or $HClO_8$
Phosphuretted hydrogen	H_3P	or H_3P
Chlorophosphoric aldehyd	$Cl_3P\Theta$	or Cl_3PO_2
Hypophosphorous acid	$H_3P\Theta_2$	or H_3PO_4
Phosphorous acid	$H_3P\Theta_3$	or H_3PO_6
Phosphoric acid	H_3PO_4	or H_3PO_8

Ethylene	$H_4 Ȼ_2$	or $H_4 C_4$
Aldehyd	$H_4 Ȼ_2 Ɵ$	or $H_4 C_4 O_2$
Acetic acid	$H_4 Ȼ_2 Ɵ_2$	or $H_4 C_4 O_4$
Glycolic acid	$H_4 Ȼ_2 Ɵ_3$	or $H_4 C_4 O_6$

Chloride of carbon	$Cl_2 Ȼ$	or $Cl_2 C_2$
Phosgene	$Cl_2 Ȼ Ɵ$	or $Cl_2 C_2 O_2$
Formic acid	$H_2 Ȼ Ɵ_2$	or $H_2 C_2 O_4$
Carbonic acid (hydrated)	$H_2 Ȼ Ɵ_3$	or $H_2 C_2 O_6$

328. Precisely as the triplication of nitrogen necessarily leads to the triplication of phosphorus and its congeners, so must the duplication of oxygen lead to the duplication of sulphur and its congeners. Every argument that applies to the duplication of oxygen applies with almost equal force to the duplication of sulphur. One important consequence arises from the duplication of the atomic weight of sulphur, namely, the necessary representation of the sulphurous and sulphuric acids as bibasic. Now, the question of basity is a purely experimental one. If we find the sulphurous and sulphuric acids to have the properties of bibasic acids, we have a strong corroboration of the high atomic weights of sulphur and oxygen. But if we should find the sulphurous and sulphuric acids to have the properties of monobasic acids, that single circumstance would be of itself almost sufficient to discredit the view which accords to oxygen the atomic weight 16, and to sulphur the atomic weight 32.

329. Gerhardt considered that 18 water, 28 carbonic oxide, 44 carbonic acid, 80 sulphuric acid, &c., are the true atomic weights of these substances, from this circumstance, that when these bodies combine with, or are given off, in the decomposition of organic bodies, the quantity of these bodies which enters into combination, or is set free, is always 18, 28, 44, and 80 respectively, or some simple multiple thereof; and not in the proportion 9, 14, 22, or 40, as he considers would be the case if these were the atomic weights of those bodies.

330. *Arguments against doubling the atomic weight of oxygen, &c.*

Professor Faraday discovered that, *if the same pair of elements form more than one compound with each other,* *it is only the compound which contains one equivalent of each element that admits of electrolysis; and that electro-chemical equivalents coincide and are the same with ordinary chemical equivalents.* He thus describes the application of this law of electrolysis to the determination of atomic weights:—"A very valuable use of electro-chemical equivalents will be to decide, in cases of doubt, what is the true chemical equivalent, or definite proportional or atomic number of a body; for I have such a conviction that the power which governs electro-decomposition and ordinary chemical attractions is the same, and such confidence in the over-ruling influence of those natural laws, which render the former definite, as to feel no hesitation in believing that the latter must submit to them also. Such being the case, I can have no doubt that, assuming hydrogen as 1, and dismissing small fractions for the simplicity of expression, the equivalent number or atomic weight of oxygen is 8; of chlorine, 36; of bromine, 78·4; of lead, 103·5; of tin, 59, &c., notwithstanding that a very high authority doubles several of these numbers." As water is an electrolyte, it must therefore consist of an atom of oxygen $= 8$, and an atom of hydrogen $= 1$. In fact, if this law of Faraday be universally true, the binary nature (composed of a single atom of each of its constituents) of a compound would be at once determined, if it was found, by experiment, to be an electrolyte.*

331. When binoxide of nitrogen, NO_2 $(O = 8)$, is acted upon with zinc-ethyl, ZnC_4H_5 $(C = 6)$, one-fourth of the oxygen $(= 8)$ in 2 atoms of the binoxide of nitrogen is replaced by the radical ethyl, C_4H_5 $(C = 6)$. In like manner, when carbonic acid, CO_2 $(C = 6, O = 8)$, is acted upon with sodium-ethyl, NaC_4H_5, one-fourth of the oxygen $(= 8)$ in 2 atoms of the carbonic acid is replaced by the radical ethyl.

332. By the adoption of the double equivalents for the members of the 2nd group (oxygen, &c.), there ceases to be any molecular analogy between the compounds of those bodies and those forming the 1st group (chlorine, &c.), as shown by the following examples:—

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* Henry's "Life of Dalton."

Protoxide of iron -	$Fe_2 O$	Protochloride of iron	$Fe Cl$
Protosulphide of iron	$Fe_2 S$	Protoiodide of iron -	$Fe I$
Sesquioxide of iron	$Fe_4 O_3$	Sesquichloride of iron	$Fe_2 Cl_3$
Sesquisulphide of iron - - -	$Fe_4 S_3$	Sesqui-iodide of iron	$Fe_2 I_3$
Arsenious acid (anhydride) - -	$As_2 O_3$	Terchloride of arsenic	$As Cl_3$
Pentoxide of antimony - - -	$Sb_2 O_5$	Pentachloride of antimony - - -	$Sb Cl_5$
Teroxide of bismuth	$Bi_2 O_3$	Terchloride of bismuth - - -	$Bi Cl_3$
Binoxide of tin -	$Sn O_2$	Bichloride of tin (the old name) - -	$Sn Cl^4$
Mercurous oxide -	$Hg_4 O$	Mercurous chloride -	$Hg_2 Cl$
Mercuric oxide -	$Hg_2 O$	Mercuric chloride -	$Hg Cl$

333. This difference between the composition of the oxides, &c., and the chlorides, &c., renders the reactions by which the one class is converted into the other class of compounds more complicated. Examples:—

Conversion of protoxide of iron into protochloride.

On the old view.	On the new view.
$Fe O + H Cl = Fe Cl + H O$	$Fe_2 O + 2 H Cl = 2 Fe Cl + H_2 O$

Conversion of sesquioxide of iron into sesquichloride.

$Fe_2 O_3 + 3 H Cl = Fe_2 Cl_3 + 3 H O$	$Fe_4 O_3 + 6 H Cl = 2 Fe_2 Cl_3 + 3 H_2 O$

Conversion of arsenious acid into terchloride of arsenic.

$As O_3 + 3 H Cl = As Cl_3 + 3 H O$	$As_2 O_3 + 6 H Cl = 2 As Cl_3 + 3 H_2 O$

Conversion of binoxide of tin into bichloride (old name).

$Sn O_2 + 2 H Cl = Sn Cl_2 + 2 H O$	$Sn O^2 + 4 H Cl = Sn Cl_4 + 2 H_2 O$

Conversion of mercurous oxide into mercurous chloride.

$Hg_2 O + H Cl = Hg_2 Cl + H O$	$Hg_4 O + 2 H Cl = 2 Hg_2 Cl + H_2 O$

Conversion of mercuric oxide into mercuric chloride.

$Hg O + H Cl = Hg Cl + H O$	$Hg_2 O + 2 H Cl = 2 Hg Cl + H_2 O$

334. The atom of a compound body, according to the new views, occupies two volumes in a state of vapour; for the relation between the atomic weight and specific gravity, in the state of vapour, has been so uniformly observed, that chemists are inclined to doubt the exactitude of the formulas of all compounds, the atomic weight of which does not yield two volumes of vapour, and the determination of the vapour-density of a compound has thus become one of the most important means of controlling chemical formulæ (116). But there are some known exceptions to this rule, of which the following are examples.

335. In the first series it will be seen that the mercuric chloride, bromide, and iodide, occupy only one volume, whilst the corresponding mercurous chloride and bromide occupy two volumes. If we make the equivalent of the metal = 200, then the mercuric, as well as the mercurous salts, would occupy two volumes of vapour. The student will notice that two volumes are condensed into one in the mercuric salts; therefore the vapour-volume of one of the elements becomes lost, as it were: and three volumes are condensed into two in the mercurous salts; the vapour-volume of one of the elements is therefore lost, as it were, by the combination.*

Name of the substance.	Density of vapour.		
	Experiment H = 1	Theory one volume H = 1	Theory two volumes H = 1
Mercuric iodide, $Hg\,I$	230·07	227	...
Mercuric bromide, $Hg\,Br$	175·96	180	...
Mercuric chloride, $Hg\,Cl$	141·81	135·5	...
Mercurous bromide, $Hg_2\,Br$	146·73	...	140
Mercurous chloride, $Hg_2\,Cl$	120·82	...	117·75

We will first give the next series, and then make some observations upon their vapour-densities.

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* The student might consult, with advantage, a paper on vapour-volumes, by Greville Williams, in the *Chemical News*, vol. i.

Name of the substance.	Density of vapour.	
	Experiment H = 1.	Theory 4 volumes H = 1.
Chloride of ammonium - - - -	12·87	12·875
Pentachloride of phosphorus - -	13·04	12·75
Hydrosulphate of the sulphide of ammonium - - - - - - - -	13·039	12·75
Hydrotellurate of the telluride of ammonium - - - - - - - -	19·1	20·5
Hydrated oxide of ethylene-diethyl-diammonium - - - - - - - -	33·2	33·3

336. Dr. Hofmann has discovered that hydrated oxide of ethylene-diethyl-diammonium, iodide of tetrethylammonium, and other analogous organic bodies, split up into two bodies at the temperature at which the vapour-density is determinable; hydrated oxide of ethylene-diethyl-diammonium splits up, for instance, into water and ethylene-diethyl-diamine, iodide tetrethylammonium splits up into iodide of ethyl and triethylamine; the consequence is, that the balloon contains not *one vapour*, occupying four volumes, but *two vapours*, each occupying two volumes.* As soon as the balloon cools, however, the two gaseous bodies recombine, and produce the original substance. These discoveries of Hofmann's render it doubtful whether any substance yields a four-volume vapour; that in those cases where a four-volume vapour is produced, whether it is not occasioned by the decomposition of the substances into two others whose vapours each occupy two volumes.

337. If a compound containing oxygen, or one of the elements whose atomic weights are doubled according to the new views, contained in two volumes of vapour, which is the measure of an atom, 8 of oxygen, or a quantity corresponding to the old atomic weights of any of the other elements whose atomic weights are now doubled, it would prove, at least, that in some cases the old atomic

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* The student is referred to Hofmann's paper for the method he adopted for proving experimentally that these bodies split up into two others. "Proceedings of Royal Society," vol. x., page 598.

weights of these bodies were correct; but no compound has yet been discovered which contains in one atom (= 2 volumes of vapour), 8 of oxygen, 16 of sulphur, &c. These elements are always present in two volumes of the compound, in the proportion of 16 of oxygen, 32 of sulphur, or in some multiple of these numbers.

338. *The different views which are held on the constitution of compound bodies.*

The different views which the old and new school of chemists hold upon the constitution of compounds, may be said to have their origin in the different views they hold upon the constitution of the following class of compounds,—the hydrated and anhydrous basic bodies; anhydrous and hydrated acids; and alcohols and ethers. We will give the constitution of caustic, and the so-called anhydrous potash, hydrated and anhydrous nitric acid, alcohol and ether, according to both views:—

	Old view. Old atomic weights.	New view. New atomic weights.
Potash - -	- KO - -	- KKO
Caustic potash -	- KO, HO -	- KHO
Anhydrous nitric acid	- NO_5 - -	- N_2O_5
Nitric acid - -	- NO_5, HO -	- NHO_3
Alcohol - -	- C_4H_5O, HO	- C_2H_6O
Ether -	- C_4H_5O -	- $C_4H_{10}O$

339. According to the ordinary or old view, compound bodies are formed of two groups of atoms, maintained in connection with one another by an electric force. They are divided, according to this view, into four classes, viz., acids, bases, salts, and indifferent bodies. That the class of bodies termed salts, are formed by the union of electro-negative bodies (acids) with electro-positive bodies (bases); and that after the union the acid and base both exist in the salt; they are supposed to be simply conjoined. This system, therefore, explains the arrangement of the atoms in a compound, or the proximate constitution of compound bodies. The combination of two compound bodies is considered to be simply the conjoining of the two together, as both are supposed to exist in the compound produced. This system is therefore called the *Dualistic system*, because compounds are regarded as formed of successive binary groups.

Examples:—Nitric acid is considered to be a compound of anhydrous nitric acid and water. Caustic potash is considered to be a compound of potash and water. Alcohol is considered to be composed of ether and water. A salt is considered to be composed of an acid and a base.

340. The constitution of compounds is determined, according to the dualistic system, by their chemical formation, and the products of their decomposition; in other words, by the phenomena of chemical reactions; and also by the substances into which they are split up when decomposed by the galvanic battery. According to this reasoning, caustic potash is composed of water and potash, because it can be decomposed into these two substances, or it can be formed by bringing these two substances together. According to the same reasoning, nitric acid is composed of $N O_5$ and $H O$, because it can be decomposed into these two substances, or it can be formed by bringing these two substances together. In the same way, salts are supposed to be made up of acids and bases, because they can be decomposed by chemical reactions, in the galvanic battery, into these two classes of compounds, or they can be formed by simply bringing these two classes of compounds together. We shall presently have to consider whether the arrangement of the atoms of a compound can be determined from the compounds out of which it is formed, or from the substances which result from its chemical decomposition.

We shall, in this paragraph, glance at the decomposition of some compounds by the galvanic current, and see whether these decompositions accord with the constitution of these bodies according to the dualistic theory. Solutions of the oxygen salts of the alkalies and alkaline earths yield the *hydrate* of the base at one pole, and the hydrated acid at the other pole of the battery. Solutions of the oxygen salts of the heavy metallic oxides yield the metal at one pole, and the oxygen and the hydrated acid at the other pole. A solution of common salt gives chlorine at the positive, and soda and hydrogen at the negative pole of the battery. Hydrate of potash yields oxygen gas at the positive, and potassium and hydrogen at the negative pole of the battery. Neither in the decomposition of these or any other compounds by the galvanic current, do *those proximate elements separate* from the decomposing substance of which, by the dualistic theory, it is considered to be composed. The reactions of the galvanic battery do not, therefore, support the constitution of bodies according to this theory; indeed, when we previously considered (225) the decompositions of the oxygen salts by the galvanic current, we saw that the reactions effected rather favoured the existence in this class of salts of a metal combined with an oxycompound of the metalloid, than of the oxide of a metal (the base) combined with an anhydrous acid.

341. I shall now endeavour to lead the student forward to the most recent views of the constitution of compounds. This, I believe, can be most thoroughly and pleasantly accomplished by giving a condensed history of the views which have been put forward, at various times, by different chemists.

342. Dr. Thomas Clark taught, in the chemical lectures he delivered in the Mechanics' Institution of Glasgow, in the year 1826, that the so-called hydrated oxygen acids did not contain water, and that the formula for water was not H O, but H O, H. The constitution of these bodies, according to Dr. Clark's ideas, was given by Mr. J. J. Griffin, in a work which he published in 1834, under the title of "Chemical Recreations;" and he gave, along with these views of Dr. Clark, his own views upon the constitution of the hydrated and anhydrous metallic protoxides, and the constitution of salts. In order to place before the student the views which Mr. Griffin then held on the constitution of bodies, I will give a few extracts from "Chemical Recreations."

343. "The difference between an *acid* and a *salt* is this,—the former contains one combining proportion of hydrogen, when the latter, instead of this hydrogen, contains exactly one combining proportion of a *metal, all other constituents*, both of the acid and salt, remaining the same.

Examples:—

S, O, H = Sulphuric acid.
S, O_2, K = Sulphate of potash.
N, O_3, H = Nitric acid.
N, O^3, K = Nitrate of potash.
C, O_2, H = Oxalic acid.
C, O_2, K = Oxalate of potash.
$Cl\ \ , H$ = Muriatic acid.

$Cl\quad, K$ = Muriate of potash.
Cl, O_3, H = Chloric acid.
Cl, O_3, K = Chlorate of potash.

"Numberless illustrations of this sort could be given, but these suffice to confirm the above proposition, viz., that the hydrated acids are simply salts of hydrogen. The reason why I wish to direct the student's attention to this subject is, that in every chemical book which falls into his hand, he will find the absurd proposition gravely inculcated that the *salts* CONTAIN *acids;* that, for example,—

Sulphate of potash *contains* sulphuric acid.
Nitrate of potash *contains* nitric acid.
Oxalate of potash *contains* oxalic acid.
Muriate of potash *contains* muriatic acid.
Chlorate of potash *contains* chloric acid.

All of which assertions are destitute of the smallest foundation in truth, and are, indeed, self-evident impossibilities. In fact, it would be quite as correct to say that sulphuric acid contains sulphate of potash, as to say that sulphate of potash contains sulphuric acid. The truth is, that they are two distinct compounds, each of which contains the same number of constituent atoms, but neither of which does, or can, form *part* of the other.

344. "The hydrate of a metallic protoxide contains one atom of oxygen, one atom of hydrogen, and one atom of metal.

345. "Every chemist but myself assumes the hydrates of metallic protoxides to consist of metallic protoxides combined with water. They make this assumption even in cases when the hydrates have been exposed, under common atmospheric pressure, to a *red heat,* without suffering decomposition, or giving off a particle of steam. But my opinion is that the hydrates of the metallic protoxides contain neither protoxides nor water, but are constituted of one atom each of metal, oxygen, and hydrogen. This is the *ultimate* constitution. What the *proximate* constitution is, I cannot tell. It may be $KH + O$, or $KO + H$, or $K + HO$; we have no means of determining *which.* I rest upon the ultimate constitution.

346. "The difference between a hydrate of a protoxide of a metal (such as slaked lime), and an anhydrous protoxide of a metal (such as quicklime), is this:—The former contains a combining proportion of hydrogen, when the latter contains a combining proportion of a metal. The difference between a hydrated protoxide and an anhydrous protoxide is, therefore, the same as the difference between an acid and a salt. In both cases, one of the compounds contains a combining proportion of hydrogen, which is replaced in the other by a combining proportion of a metal.

Example:—

$\mathrm{Ca, H, O}$ - -	Hydrate of lime
$\mathrm{Ca, Ca, O}$ - -	Anhydrous lime

347. "This is the case with all the metallic protoxides. It is needless to encumber the reasoning with illustrations.

348. "These hydrates of protoxides contain no water, for they contain but one proportion of hydrogen, whereas water contains two proportions. Yet they give off water when exposed to heat, and they produce nothing else than anhydrous protoxides. There is no difficulty in ascertaining how this effect is produced, or in showing the source of the constituents from which the water is *produced* by this experiment:—

Two proportions of hydrate of lime.	What they produce by exposure to heat.
$\mathrm{Ca\,H\,O}$	$\mathrm{Ca\,Ca\,O}$
$\mathrm{Ca\,H\,O}$	$\mathrm{H\,H\,O}$

349. "It boots not that we know how many elementary atoms of the different elements composing a compound are contained in that compound. These are but the *ultimate* constituents; and what we want to know is, how these are combined together into *proximate* constituents. This is a problem for future times to solve, and it is a problem of that importance that we are not warranted in *assuming* its solution, merely for the purpose of grounding a nomenclature and a system of arrangement upon the assumed solution. Yet this is done in the antiphlogistic nomenclature and theory. It is assumed that sulphate of baryta contains baryta and sulphuric acid, that nitrate of potash contains potash and nitric acid, that caustic soda contains protoxide of sodium and water; and these assumptions

form the groundwork of the French theory and nomenclature—the groundwork of the theory adopted by the gifted Berzelius, who has spent twenty years in vain attempts to establish it. The root of the system of this chemist is, that in the sulphate of lead the oxygen is so divided between the sulphur and the lead, that the portion combined with the former bears to the portion combined with the latter the ratio of 3 to 1. I hesitate not to say, that *this is an assumption incapable of proof*.

350. "Let us examine the formation of sulphate of lime with a view to discover its proximate constituents:—

"1st. When 4 parts of sulphur are converted into sulphuric acid by digestion with nitric acid, and the solution is precipitated by a solution of lead, the resulting sulphate of lead weighs 38, containing 26 of lead, and consequently 8 of oxygen.

"2nd. When 26 parts of lead are dissolved in nitric acid, and the solution is precipitated by sulphuric acid, or by the solution of a sulphate, the resulting sulphate of lead weighs 38, containing 4 of sulphur, and 8 of oxygen.

"3rd. When 30 parts of sulphuret of lead, containing lead 26, and sulphur 4, are converted by oxidation into sulphate of lead, the weight of the product is 38, including 8 of oxygen.

"4th. When 35 parts of chloride of lead, which contain chlorine 9, and lead 26, are precipitated by sulphuric acid, the resulting sulphate of lead weighs 38, and contains 4 of sulphur and 8 of oxygen.

"5th. When 30 parts of brown oxide of lead, which contains lead 26, oxygen 4, are exposed to an atmosphere of sulphurous acid gas, they absorb 8 parts of that acid, equal to oxygen 4, and sulphur 4, and produce 38 parts of sulphate of lead.

351. "The information afforded by the above experiments is, that sulphate of lead is composed of—

Lead - - - -	26
Sulphur - - - -	4
Oxygen - - - -	8
	38

But none of these experiments afford the least insight into the manner in which these elements are combined together. The assumption that one-fourth of the oxygen is combined with the lead, and three-fourths with the sulphur, is perfectly gratuitous.

352. "The most direct of the whole five experiments (5th) is in favour of the conclusion, that sulphate of lead is PbO, SO; a conclusion very different from that which Berzelius comes to, but which agrees precisely with my opinion that 26 parts of lead is the quantity which is equivalent in combination to a volume of hydrogen.

353. "It is very well to admit the doctrine of proximate constitution in theory, because it is useful in explaining a variety of phenomena, such as chemical combinations, electrical decompositions, and the like. But when we come to arrange the products of chemistry into a system, and to give them systematic names, the only safe way to view them is in relation to their ultimate constitution. It is only by founding a nomenclature upon this basis, that we can hope to avoid the perplexities which arise from the *guess-work* of the proximatists.

354. "But, it may be said, in rejecting proximate constitutions, and stating only the ultimate constitution of compounds, you give false notions of secondary compounds, the properties of which depend upon the nature of their proximate constituents. Thus, sulphate of baryta derives its properties from the sulphuric acid and baryta which compose it.

355. "I reply, No; sulphate of baryta derives its properties from the barium, sulphur, and oxygen which compose it, just as sulphuric acid and baryta, considered as distinct compounds, derive their properties from the same ultimate elements. In short, viewed in any light, it is the ultimate elements which determine the character of the compounds. There is a fashion, but no utility, in assuming proximate constitution as the basis of a systematic nomenclature.

356. "I think that the word ACID, taken as a substantive name, ought to be disused in chemistry. It has done mischief. It ought to be employed only as denoting a quality."

357. The elements of a compound may be brought together in a variety of ways, yet the same compound will be produced, provided its constituents are only present in the right proportions; and a compound can also be decom-

posed in a variety of ways, the substances into which the compound is resolved varying with the mode of decomposition. Thus a sulphate may be produced from a metal and the so-called hydrated acid; or from the oxide of a metal and the anhydrous acid; or from the binoxide of the metal and sulphurous acid; or from the sulphide of the metal and oxygen; and a sulphate might, in different ways, be decomposed into these different substances: the proximate elements of a compound cannot therefore be ascertained, either from the substances out of which the compound is formed, or from the substances into which it is decomposed, as the *dualistic* theory requires.

358. *The unitary system of M. Gerhardt.*—Some years after Mr. Griffin had published his views upon the constitution of water, the anhydrous and hydrated acids, the anhydrous and hydrated bases, Mr. Gerhardt published similar views, and employed the same line of argument as Mr. Griffin has done, with the exception that he used sulphate of baryta instead of sulphate of lead to illustrate the impossibility of discovering the arrangements of the atoms of a compound, either from the substances out of which it can be formed, or from the substances into which it can be decomposed. He, like Mr. Griffin, considered all chemical compounds as SALTS, which are formed of a metal and a non-metallic body, and which can be exchanged by double decomposition; hydrogen he included amongst the metals, when it could be exchanged in its compounds for a metal; he therefore classed along with the bodies which other chemists recognised as salts the hydrated acids, water and the bases. As he reduced all formulæ to one common standard, the formulæ being derived one from the other by substitution, he called his system of notation "THE UNITARY SYSTEM." Formulæ in the unitary system "were framed in accordance with the following hypothesis; namely, that salts do not consist of acids and bases; that we know nothing of the proximate constitution of salts; that it is impossible to determine in what manner the atoms of the ultimate elements of salts are grouped together; that, consequently, the construction of dualistic formulæ, which affect to explain the constitution of salts, is unwarranted, and, finally, that the symbols composing each formula should be made to represent only a single molecule."

359. M. Gerhardt thus explains the unitary system in the preface to his work entitled, "Introduction to the Study of Chemistry by the Unitary System." This book contains an essay of reform which I submit to the judgment of chemists; it contains a new system, and a new method of instruction, the application of which to chemistry appears to me advantageous with respect to the progress of science, as also to that of instruction.

360. In examining with honesty the general system of instruction, one is forced to notice, that it notonly does not give rigorous definitions, but that it too often makes use of hypothetical bodies in the interpretation of phenomena.

361. In the system which I propose for adoption, all the bodies are considered as unique molecules, whose atoms are disposed in a determinate order, which the chemical reactions indicate only in a *relative manner*.

362. The dualistic system assimilates, on the contrary, all chemical compounds to oxides or to salts, and attributes an absolute value to the formulæ which represent their composition. These formulæ, in my opinion, only trace out the meaning of one or two reactions; they never give the true image of the molecular constitution; they only express, I repeat, the simple relation or resemblance.

363. In the dualistic system, we explain or define things which do not even exist; this method is incompatible with the unitary system. This, in effect, takes its definition from the metamorphosis of bodies, that is to say, from their decomposition or from their formations, and, under this relation, it responds evidently to the especial aim of chemistry, which is the study of the laws of the transformation of matter.

364. Some examples are given in order to comprehend this difference. The dualistic system gives the name of salts to bodies which are composed of an acid and a base; but there are numberless exceptions to the rule. In the unitary system, we call all bodies containing a metal, which can be exchanged by double decomposition for another metal, a salt; that is to say, all bodies capable of undergoing such a characteristic metamorphosis.

365. The dualistic system calls *alcohol*, the combination of a compound radical of carbon and hydrogen with oxygen, with which water is united: I define the alcohols in this way; they are composed of carbon, hydrogen, and

oxygen; they are capable of abandoning the elements of water for converting themselves into a combination of n $C H_2$, and of exchanging H_2 for O in order to become monobasic acids n $C H_2 + O_2$.

366. The dualistic system calls certain bodies *amides;* and, according to this, they contain amidogen, which is an hypothetical body. In the unitary system, the denomination amide is applied to the bodies susceptible of conversion into ammoniacal salts by the fixation of the elements of water.

367. Before giving a few more extracts from Gerhardt's book on the unitary system, we will place before the student the arguments which Laurent adduced to show—1st. That there is no analogy between the anhydrous and hydrated acids. 2nd. That the so-called hydrated acids do not contain water.

1st. The anhydrous and the hydrated acids are always confounded, and employed, theoretically at least, the one for the other. Nevertheless, these bodies do not present any analogy; under no circumstances whatever do they comport themselves in the same manner; their functions are entirely different. Take, for example, the anhydrous sulphuric acid and the sulphate of hydrogen (hydrated sulphuric acid). The first does not combine with metals; the second does combine with them, at the same time liberating hydrogen. The first unites directly with the metallic oxides; the second gives rise to a double decomposition. The first does not decompose chlorides, and even combines with some of them; whereas the second decomposes them. The first, by acting upon the anhydrous carbonate of ammonia, does not give rise to the sulphate of ammonium; but the second does. The first forms, with the volatile alkaloids, amides or amidic acids; the second gives rise to salts. The first combines with chloride of ammonium; the second decomposes it. The first behaves in one manner with the alcohols, amides, and hydrocarbons; the second behaves in another. The parallel may be pursued as far as we please, and under no circumstances shall we discover any analogy between the reactions. If, in opposition to this opinion, any one were to advance the decomposition of carbonate of potash by the anhydrous and the hydrated sulphuric acids, I would ask in reply, if the action of *oxamide* upon potash is the same as that of *oxalate of ammonia* upon the same base, and whether it is always necessary to neglect, on account of its cheapness, the water which is added or eliminated?

The anhydrous and the hydrated acids, then, have not any analogy with one another, and ought to be placed in two perfectly distinct classes. Nevertheless, it is not without reason that chemists have associated them together. It is indeed true that these bodies are not without some community of properties; but the relations which exist between them are of the same order as those which exist between the sulphide of copper and its sulphate,—between sulphuric acid and sulphur,—between anhydrous sulphuric acid and sulphate of potash,—between an integrant molecule and its constituent molecules, but nothing more.

The above relations have nothing in common with the relations we observe between sulphur, selenium, and tellurium,—between the sulphurous and the selenious acids, —between the sulphate of potash and that of sulphate of soda. The bodies of the former class are associated with one another by the presence of sulphur in each of them. The bodies of the second class are correlated by a similitude of functions.

The anhydrous and the hydrated sulphuric acid have this in common,—they both contain sulphur and oxygen; but with regard to analogy of properties, they do not manifest any whatever.

2nd. Up to the present time, chemists have admitted that the oxidized compounds which give rise to salts contain a quantity of water, which corresponds exactly to their capacity of saturation. They admit, on the other hand, that oxamide, carbamide, benzamide, &c., do not contain water.

Latterly, however, we have succeeded in obtaining, with several amides, a considerable number of salts. We should conclude, from the composition of these salts, that the amides do contain water, which water represents exactly their capacity of saturation. So far there is nothing contrary to the dualistic theory, only we perceive that we have been in error concerning the formulæ of the amides, and that these compounds do contain water, and that oxamide has for its formula,—

$(C_2O, H_2N_2)\ H_2O$;

and carbamide— $(C\,H_2N_2)\ H_2O$.

But we can also combine amides with acids, without the amides experiencing any loss of water. Thus, asparagine and glycocine, on the one hand, exchange an atom of water for an atom of oxide, and, on the other hand, combine with acids without losing any water whatever. Now we know that all the hydrated organic bases, or the oxides of the different ammoniums (oxides of tetrethylium, or tetramethylium), always combine, in the anhydrous state, with acids; consequently, we conclude that asparagine, glycocine, and the amides, do not contain water. But if oxygenized bodies, such as the amides, although not containing water, can yet give rise to salts, why do we suppose that water is necessarily contained in the sulphuric, formic, and acetic acids? Here are other facts. Citric acid is tribasic, and consequently contains, according to the dualistic doctrine, three atoms of water. By cautious heating, it can be made to lose one of these three atoms. Will it have then become bibasic? Not at all. We put it into contact with three atoms of potash, and although it only contains two atoms of water ready formed, yet it disengages three atoms thereof in order to take up the three atoms of potash.

Isatinic acid is monobasic, consequently it contains $C_{16}H_{12}N_2O_3, H_2O$. We can cause this body to give up, not only the atom of ready-formed water, but also another atom, which is produced at the expense of the anhydrous acid. There remains, then, a neutral compound isatine, $C_{16}H_{10}N_2O_2$, which certainly cannot any longer contain water. Nevertheless, put into contact with oxide of potassium, it seizes upon this base, and abandons yet another atom of water. I will not say that all these reactions are impossible, but simply that they are in the highest degree improbable, and that the only means we have for explaining all these reactions consists in a simple admission of this fact, namely, that sulphuric, formic, acetic, citric, and isatinic acids, isatine, asparagine, glycocine, &c., are capable of exchanging 1, 2, or 3 equivalents of hydrogen for 1, 2, or 3 equivalents of potassium, lead, copper, &c., without supposing that the hydrogen necessarily existed in the state of water.

368. M. Gerhardt, in the work to which we have already alluded, after showing that sulphate of baryta can be produced, as Mr. Griffin had with regard to sulphate of lead, from anhydrous sulphuric acid and baryta; from sulphurous acid and peroxide of barium; from sulphide of barium and oxygen; as well as from ordinary sulphuric acid and baryta; concludes thus:—The only thing without any doubt is the proportional weights of sulphur, of barium, and of oxygen contained in the sulphate of baryta, in whatever way it may have been produced. In effect, we have—

$$\begin{aligned} S\,O_3 + O\,Ba_2 &= S\,O_4\,Ba_2 \\ S\,O_2 + O_2\,Ba_2 &= S\,O_4\,Ba_2 \\ S\,Ba_2 + O_4 &= S\,O_4\,Ba_2 \end{aligned}$$

369. Moreover, if the elements of sulphate of baryta are found in presence of each other in the proportions required, whether in one form or another, we conceive that the most powerful combination will be formed, provided that we place the whole of these elements in the most favorable circumstances.

370. One and the same body can be produced by more than one metamorphosis; the chemical reactions do not indicate the molecular disposition, or the constitution of the bodies. They only make known in a positive manner the simple numerical proportions between the different elements.

371. Without doubt, the difference in bodies is not due alone to the quality or quantity of the constituent elements; we have already said, the order in which the particular materials are disposed, plays, in the chemical phenomena, a part not less important than that performed by the nature and the number of the components. But the metamorphoses never teach this order in an absolute manner. When we compare the metamorphoses of two similar compounds—for example, sulphate of baryta and sulphate of lime, they conduct only to a relative appreciation of the molecular order; they suggest only—

If sulphate of baryta is - $S\,O_3 + O\,Ba_2$
Sulphate of lime - - $S\,O_3 + O\,Ca_2$

Or else that—

If sulphate of baryta is - $S\,O_4 + Ba_2$
Sulphate of lime - - $S\,O_4 + Ca_2$

372. The knowledge of the absolute molecular arrangement in a body evidently supposes that all the metamorphoses that can take place have been discovered. This has not yet been accomplished, and before it can be realised, the science must be considerably extended. Moreover, over and above the chemical metamorphoses, it is necessary also to study the physical characters of bodies, and note the relations which exist between their composition and their crystalline form. We possess at present, in this respect, only isolated facts; useful without doubt, but from which we cannot yet draw general consequences in favour of the molecular order of all bodies.

373. *Williamson's reasons for considering that many bodies are formed on the type of water.*—Since the time that Gerhardt proposed his unitary system of chemistry, the views of chemists on the *constitution of bodies* have been, in some degree, altered by the experiments of Dr. Williamson on the mode by which the alcohols are transformed into ethers. Williamson was led to institute these experiments from the opinion he had formed that the alcohols and ethers were formed on the type of water; and as his experiments confirmed this view of the constitution of these bodies, he considered that many other bodies besides the alcohols and ethers were formed on the water type. Before we describe more at length this view of the constitution of bodies according to types, we must place before the student the different views which have been, and are, held on the constitution of the alcohols and ethers, and the different theories which have been proposed to account for the transformation of alcohols into ethers.

374. *The different views held on the constitution of the alcohols and ethers, and the different theories of etherification.*—Gay Lussac first threw out the suggestion that ether and alcohol are different hydrates of olefiant gas; ether being the monohydrate, alcohol the bihydrate. According to this view, which was adopted by Dumas and Bolley, the compounds of the oxygen acids and ether are compounds of the first hydrate with oxygen acids; and the etherial bodies formed by the action of the hydrogen acids upon ether are compounds of those acids with olefiant gas; ether, alcohol, acetic ether, and hydrochloric

ether, have the following rational constitution according to this view:—

Ether - - -	C_4H_4, HO
Alcohol - - -	$C_4H_4, 2HO$
Acetic ether - -	$(C_4H_4, HO) + C_4H_3O_3$
Hydrochloric ether -	C_4H_4, HCl

375. Sir Robert Kane was the first to regard ether as the protoxide of the compound radical C_4H_5 (which he called ethereum). Berzelius and Liebig both adopted Kane's view of the constitution of ether; and Berzelius proposed to regard alcohol as the oxide of the radical (C_2H_3); whilst Liebig regarded alcohol as the hydrate of the oxide of ethyl.

376. The relationship which exists, according to Liebig's view, between the ethers and alcohols, was considered to be completely proved by the way in which a great many of the ethers can be produced from the corresponding alcohols. Many acids and salts, such as sulphuric acid, phosphoric acid, arsenious acid, fluoride of boron, the chlorides of tin and zinc, and other chlorides, are capable, at certain temperatures, of removing water from some of the alcohols, which become transformed, by this removal, into the corresponding ethers. But although water is removed from the alcohol by these bodies, and the alcohol becomes converted into ether by the removal of water, it does not follow that the water exists as such in the alcohol, as sulphuric acid, and these other bodies, have the power of removing from some substances containing hydrogen and oxygen these elements, in the proportion to form water. In fact, alcohol cannot be converted into ether by adding to it substances like chloride of calcium, which possess a strong affinity for water; nor can ether be made to combine directly with water; but, if alcohol and ether were related in the way Liebig's theory supposes, we should expect to convert alcohol into ether by the mere removal of water, and that ether ought to combine directly with water to form alcohol.

377. The best process for preparing ether from alcohol is as follows:—5 parts of alcohol, of at least 90 per cent., are mixed with 9 parts of sulphuric acid, and the mixture is introduced into a retort and rapidly heated to the boiling-point, at which temperature it is kept during the

whole of the operation. During the whole of the distillation, fresh alcohol is constantly flowing into the retort from a vessel fitted with a stop-cock, to which is attached a bent glass tube; this tube passes through the tubulure into the retort, and is fitted into the tubulure by means of a perforated cork. The alcohol is made to flow into the retort as fast as the ether, &c., distils over; the liquid in the retort is, therefore, kept at the original level throughout the operation. The distillate is condensed in a powerful Liebig's refrigeratory; it consists chiefly of ether, with water in such proportions as would convert the ether into alcohol, and a very little alcohol, sometimes none at all. The operation may be advantageously continued until 31 parts of alcohol at 90 per cent. have flowed into the retort, and, of course, an equal quantity of ether and water has distilled over. The oil of vitriol remains behind in the retort, in combination with a larger quantity of water than it was originally combined with, but a part of the acid is united with the elements of the alcohol, forming an acid ($C_4 H_5 O, 2 SO_3 + H O$) called sulphovinic acid.

378. Two different views have been held as to the cause of the resolution of the alcohol into water and ether, and as to the nature of the transformation. Liebig, and the majority of chemists, believe that etherification is produced by means of the chemical force, and that the alcohol is first transformed into sulphovinic acid, which is decomposed by the heat into ether, sulphuric acid, and water; and that as soon as the acid is set free by the decomposition of the sulphovinic acid, it again unites with a fresh portion of alcohol, forming sulphovinic acid, which is again decomposed, so that the formation and decomposition of the sulphovinic acid goes forward continuously; this is one of the views. The other view, which is supported by Mitscherlich, Berzelius, Graham, and others, considers that etherification is effected by means of the catalytic force, and that the sulphuric acid decomposes the alcohol into ether and water immediately.

379. The first, or Liebig's view, is considered to be supported by Hennell's discovery, "that sulphuric acid, diluted with so much water that it will not form sulphovinic acid with alcohol, is likewise incapable of converting alcohol into ether by distillation," but this appears to me

to be no proof, as sulphuric acid, so diluted as to be incapable of forming sulphovinic acid, may also, on account of its dilution, be incapable of removing the elements of water from the alcohol, and thus transforming it into ether. As long as the alcohol is admitted, the ether is formed; if, then, the alcohol is first converted into sulphovinic acid, and the ether is formed from the decomposition of this acid, the formation of the acid must precede the formation of the ether throughout the entire period of the process; the difficulty then arises of explaining why the sulphovinic acid is formed and decomposed at the same temperature. Many explanations have been given, but the only one which appears to me at all entitled to attention is this,—That at the point where the alcohol enters the liquid in the retort the alcohol is in excess, and therefore, by the influence of mass, displaces or expels the water from the surrounding hydrated sulphuric acid, by combining with the acid, forming with it sulphovinic acid, which is decomposed into ether, sulphuric acid, and water, when it diffuses through the liquid in the retort, because the hydrated sulphuric acid is in excess. Mitscherlich found that one-fifth of the alcohol which enters passes off uncombined with the ether vapour; now it is perfectly consistent with the explanation of etherification just given, that part of the alcohol should remain uncombined.

380. Mitscherlich's contact, or catalytic theory, simply assumes that sulphuric acid, without being decomposed, or entering into combination, has at a high temperature the power of separating alcohol into ether and water; he considers that the sulphovinic acid which is formed is merely a secondary product, and by no means essential to the formation of the ether. This view has been strengthened by some elegant experiments of Graham; he added in a gradual manner, so as to prevent any considerable rise of temperature, one volume of oil of vitriol to four volumes of alcohol of a density of ·841; the mixture was subsequently sealed up in a glass tube of one inch in diameter and 6·6 inches in length, of which the liquid occupied 5·2 inches, a space of 1·4 inches being left vacant to provide for the expansion of the liquid by heat. The tube was placed in a digester containing water, and exposed to a temperature ranging from 284°

to 352° F., for one hour. The liquid divided by the heating into two columns; the upper, which occupied 1·75 inches in the tube, was ether; the lower, which occupied 3·5 inches, contained some ether, but was principally a mixture of alcohol, water, and sulphuric acid; it contained no sulphovinic acid, for the salt which was formed by neutralizing the acid-solution with a carbonate did not blacken when heated.

381. "The principal points to be observed in this experiment are, its entire success as an etherizing process, without distillation, without sensible formation of sulphovinic acid, and with a large proportion of alcohol in contact with the acid, namely, two equivalents of the former nearly to one of the latter. When the proportion of the alcohol was diminished, the results were not so favorable."

382. Graham found that crystals of bisulphate of soda, containing a slight excess of acid, etherized about twice their volume of alcohol when heated in a sealed tube to a temperature ranging from 284° to 352° F.; the lower liquid, in this case, contained a minute quantity of sulphovinic acid.

383. The following were some of the conclusions which Graham drew from his experiments:—that the formation of sulphovinic acid appears not to be a necessary step in the production of ether; that it appears the conversion of alcohol into sulphovinic acid diminishes its chance of afterwards being transformed into ether; for when Graham increased the proportion of oil of vitriol, so that much sulphovinic acid would be formed, the formation of ether rapidly diminished. He considers that the action of sulphuric acid upon alcohol is similar to its action upon turpentine. Oil of turpentine, mixed with one-twentieth of its volume of sulphuric acid, undergoes an entire change, being chiefly converted into a mixture of two other hydrocarbons, terebine and colophine, one of which has a much higher boiling-point and greater vapour-density than the oil of turpentine. This hydrocarbon does not combine with the acid; it has the same per-centage composition as the oil of turpentine, but it has a higher atomic weight, and greater vapour-density; the action of the sulphuric acid is therefore what may be termed a polymerizing action, as this hydrocarbon and oil of turpentine are *poly-*

meric substances. So of the hydrocarbon alcohol, its density is doubled in ether, by the same polymerizing action. The sulphovinic acid which is formed from the mixture of sulphuric acid and alcohol (which is placed in the retort, when ether is made by the continuous process) Graham considers to be the agent which polymerizes all the alcohol afterwards introduced into the fluid. Graham states, in his paper recording these experiments, "that this view of etherification is only to be considered as an expression of the contact-theory of that process which has long been so ably advocated by M. Mitscherlich."*

384. We have now to explain Dr. Williamson's views and experiments. We have seen that the formula of alcohol, according to one view, is C_2H_3O, and that two atoms of it are needed to form one of ether; one atom of the alcohol taking C_2H_2 from the other atom, water being set free; whereas, according to the other view, the proximate constituents of alcohol are ether and water. Now the question which presented itself to Williamson was this—which of these two views of the constitution of alcohol is the correct one, and could any direct fact be discovered which would solve the problem? He devised the following beautiful experiments, by which he discovered the true constitution of the ethers and alcohols.

1st Experiment.—He added ethylate of potash (C_4H_5O, KO) and iodide of ethyle, C_4H_5I, together; double decomposition ensued, ether and iodide of potassium were formed. The question arose, which of the two following decompositions took place between the ethylate of potash and iodide of ethyle:—

$$C_4H_5O,\ KO + C_4H_5I = 2\,C_4H_5O + KI;\ \text{or,}$$
$$C_4H_5O,\ KO + C_4H_5I = C_8H_{10}O_2 + KI.$$

Did the ethyle, C_4H_5, from the iodide of ethyle, unite with one of the atoms of oxygen in the ethylate of potash? If so, it would prove that the alcohols were ether plus water. Or did the ethyle in the iodide of ethyle become united with the ethyle and the two atoms of oxygen in the ethylate of potash, and form with them one indivisible atom? In that case the empirical formula must be $C_8H_{10}O_2$, and alcohol could not be the hydrate of ether. By this experiment it could not be decided which was the correct formula for ether.

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* "Observations on Etherification," by Thomas Graham, F.R.S., *Quarterly Journal of the Chemical Society*, vol. iii.

2nd Experiment.—Williamson next added ethylate of potash and iodide of methyl (C_2H_3I) together in equivalent proportions, and he obtained, not vinic ether and methyl ether, thus,—

$$C_4H_5O, KO + C_2H_3I = C_4H_5O + C_2H_3O + KI,$$

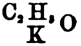
as would have been the case if the alcohols were ether plus water; for the methyl would have had, in that case, the oxygen of the water to itself; but he obtained a new ether, whose empirical formula was $C_6H_8O_2$. The mode of its formation shows that the ethyl and methyl are united in equivalent proportions, and its rational formula is therefore $(C_4H_5. C_2H_3) O_2$.

385. The formation of ethers from alcohols is made known by these experiments. They prove that the alcohols do not contain either the ethers or water; that the ethers are therefore not produced from the alcohols by the separation of these latter bodies into the ethers and water, but that the ethers are produced from the alcohols by the substitution of a compound radical for the hydrogen the alcohols contain. Williamson, in fact, made these experiments with the view of obtaining new ethers by substituting carburetted hydrogen for hydrogen in a known alcohol.

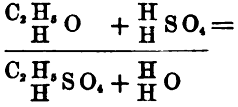
386. "Water is therefore formed in etherification by replacing the carburetted hydrogen of alcohol by hydrogen, which, of course, obliges us to assume the same unity of oxygen in both. Alcohol is therefore water in which half the hydrogen is replaced by carburetted hydrogen, and ether is water in which both atoms of hydrogen are replaced by carburetted hydrogen;" they may therefore be formulated thus—($C = 12$ and $O = 16$):—

Water.	Alcohol.	Vinic ether.	Methyl ether.
$\begin{matrix}H\\H\end{matrix}O$	$\begin{matrix}C_2H_5\\H\end{matrix}O$	$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}O$	$\begin{matrix}CH_3\\C_2H_5\end{matrix}O$

Ethylate of potash, and iodide of ether, are represented, according to this view, thus (adopting the new atomic numbers):—

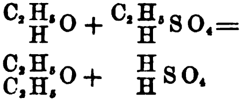
Ethylate of potash.	Iodide of ethyl.
 $\begin{matrix}C_2H_5\\K\end{matrix}O$	C_2H_5I

387. Williamson thus explains the process of etherification:—The next thing to be done is to explain the process of etherification by the action of sulphuric acid, $\begin{matrix}H\\H\end{matrix}SO_4$ upon alcohol; and in order to accomplish that, we must show the connection between those substances and the reagents used in the above-described experiments. With this view, we have merely to add to the above facts the acknowledged analogy of the simple and compound radicals in their compounds. It must first be shown how a substance analogous to the iodide of ethyl is formed, and then how, by double decomposition with alcohol, it produces ether. This is very easy; for sulphovinic acid is strictly analogous to iodide of ethyl plus iodide of hydrogen, which we should obtain by replacing SO_4 in its formula by an equivalent of iodine; and in order to represent the formation of this sulphovinic acid, which is well known to precede that of ether, the simplest mode is at the same time the one most free from hypothesis; it consists in stating the fact, that sulphuric acid and alcohol are transformed into sulphovinic acid and water, by half the hydrogen of the former changing places with the carburetted hydrogen of the latter; thus:—



$$\frac{\begin{matrix}C_2H_5\\H\end{matrix}O + \begin{matrix}H\\H\end{matrix}SO_4 =}{\begin{matrix}C_2H_5\\H\end{matrix}SO_4 + \begin{matrix}H\\H\end{matrix}O}$$

Now, from this point it is clear that the process is the same as in the decomposition above described; for, by this sulphovinic acid coming in contact with an atom of alcohol, it reacts exactly in the same manner as the iodide did, forming, of course, sulphuric acid and ether:—



$$\begin{matrix}C_2H_5\\H\end{matrix}O + \begin{matrix}C_2H_5\\H\end{matrix}SO_4 =$$
$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}O + \begin{matrix}H\\H\end{matrix}SO_4$$

388. The sulphuric acid, thus reproduced, comes again

in contact with alcohol, forming sulphovinic acid, which reacts as before; and so the process goes on continuously, as found in practice.

389. According to Mitscherlich, the sulphovinic acid plays no part, directly or indirectly, in the process of etherification; it is merely a secondary product. According to Graham, the sulphovinic acid is the polymerizing agent, therefore the sulphovinic acid, which is formed at the commencement of the operation, as it undergoes no decomposition according to his view, will *exist* at the end of the operation; whereas, according to Williamson, the sulphovinic acid is constantly changing, being decomposed as rapidly as it is formed; therefore, what remains at the termination of the process will not be that which was formed at the commencement. Williamson proved that the sulphovinic acid existing at the end of a long process of etherification was not the same as that which was formed at the first. He proved this point by making sulphuric acid react successively upon two alcohols, so that it took the hydrocarbon from the first and gave it up to the second, forming an intermediate ether; and finding only the second alcohol to react upon, remained at last combined with its hydrocarbon alone. The experiment was performed in the following manner:—sulphamylic acid, $\begin{matrix}C_5H_{11}\\H\end{matrix}SO_4$, was prepared by the action of sulphuric acid upon its equivalent weight of fusel oil, and this compound was treated with vinic alcohol by the continuous process until the distillate consisted of pure vinic ether, $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}O$. The residue was then examined, and found to contain *no* sulphamylic acid, but only sulphovinic, the mixed ether, amyl ethyl, $\begin{matrix}C_2H_5\\C_5H_{11}\end{matrix}O$, which was formed, being easily separated out from the first portions of the volatile product.

390. By oxidation, the alcohols are converted into acids. The acid produced by the oxidation of vinic alcohol is the one best known to the non-scientific. It is called acetic acid. Vinegar is acetic acid, more or less impure or diluted. According to the old view of the proximate constitution of bodies, and retaining the old atomic numbers of carbon and oxygen, the formula of acetic acid is

$C_4H_3O_3, HO$. According to this view, the ordinary acid is the hydrate of an anhydrous acid, $C_4H_3O_3$, which had not been obtained when Williamson published his views and experiments on the alcohols and ethers, and which we have just explained. Adopting the old view of alcohol and acetic acid, the former is converted into the latter by the substitution of two atoms of oxygen for two atoms of hydrogen, thus:—

$$C_4H_5O, HO + 4O = C_4H_3O_3, HO + 2HO.$$

391. Williamson, in his paper on etherification, put forward the following view on the constitution of acetic acid, which was afterwards confirmed, as we shall see presently, by the beautiful experiments of Gerhardt. "Now, as acetic acid is formed from alcohol, by replacing one-third of its hydrogen by oxygen, and viewing alcohol as water in which half the hydrogen is replaced by ethyle, $\begin{matrix} C_2H^5 \\ H \end{matrix} O$, we shall consider acetic acid as containing one equivalent of oxygen in the place of two atoms of hydrogen. Acetic acid, therefore, differs from alcohol by containing, instead of ethyle, this other radical, differing from it by having oxygen in lieu of an equivalent of hydrogen, and which may be called *oxygen-ethyle* or *othyle. If the two atoms of hydrogen in water were replaced by this othyle, we should have anhydrous acetic acid,* $\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix} O$. *In fact, the so-called anhydrous acids are nothing else than the ethers of the hydrated acids.*"

392. We are unable to place before the student any part of Williamson's paper on the constitution of salts; we must therefore refer him to the paper itself. We will simply quote the last paragraph in his paper on etherification. The method here employed of stating the rational constitution of bodies by comparison with water, seems to me to be susceptible of great extension; and I have no hesitation in saying that its introduction will be of service in simplifying our ideas, by establishing a uniform standard of comparison by which bodies may be judged of.*

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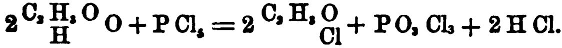
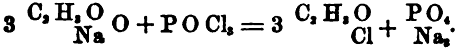
* We strongly recommend the student to peruse the following important papers by Williamson:—"Suggestions for the Dynamics of Chemistry, derived from the Theory of Etherification."—*Chemical Gazette*, vol. ix. "On the Constitution of Salts."—*Chemical Gazette*, vol. ix. "Theory of

393. Cahours discovered the chlorides of the oxygenized radicals of the organic acids. He obtained them by the action of pentachloride of phosphorus upon the so-called hydrated acids. The following changes ensue when the phosphorus compound acts upon acetic acid, and a similar decomposition takes place when it acts upon the other acids.



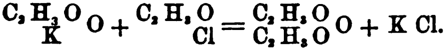
$$2\begin{array}{c}C_2H_3O\\H\end{array}O + PCl_5 = 2\begin{array}{c}C_2H_3O\\Cl\end{array} + PO,Cl_3 + 2HCl.$$

Before showing how Gerhardt applied this discovery in the production of the acid anhydrides, we will just show the student another and readier way of obtaining these chlorides, which was discovered by Gerhardt himself. If we distil acetate of sodium with oxychloride of phosphorus, the following changes ensue:—



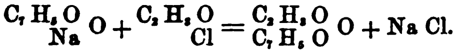
$$3\begin{array}{c}C_2H_3O\\Na\end{array}O + POCl_3 = 3\begin{array}{c}C_2H_3O\\Cl\end{array} + \begin{array}{c}PO_4\\Na_3\end{array}.$$

394. Gerhardt, by acting upon fused acetate of potassium with the chloride of othyl, obtained the acetic anhydride, thus:—



$$\begin{array}{c}C_2H_3O\\K\end{array}O + \begin{array}{c}C_2H_3O\\Cl\end{array} = \begin{array}{c}C_2H_3O\\C_2H_3O\end{array}O + KCl.$$

This method is of general applicability for the isolation of the acid anhydrides. Gerhardt also obtained mixed anhydrides, corresponding to the mixed ethers obtained by Williamson. He obtained benzoic acetate by acting upon benzoate of sodium with chloride of othyl (the other mixed anhydrides were obtained in a similar way), thus:—



$$\begin{array}{c}C_7H_5O\\Na\end{array}O + \begin{array}{c}C_2H_3O\\Cl\end{array} = \begin{array}{c}C_2H_3O\\C_7H_5O\end{array}O + NaCl.$$

When this body is subjected to distillation, it decomposes

Etherification" (page 106); "On Etherification" (page 229).—In the *Quarterly Journal of the Chemical Society*, vol. iv. In these memoirs, Williamson employs the four-volume system of Gerhardt (See par. 279).

T. S. Hunt, in a paper on the "Theory of Types in Chemistry," which the student may consult with advantage (*American Journal of Science*, vol. xxxi.), claims for Laurent the idea that alcohol may be looked upon as water in which ethyl replaces one atom; and that ether is water in which the two atoms of hydrogen have been replaced by two atoms of ethyl. Mr. Hunt claims for himself the extension of this idea of types, the credit of which is universally assigned to Williamson and Gerhardt. (See the note at the end of this chapter.)

at about 150° C. into acetic anhydride, which distils over, and benzoic anhydride, which remains behind in the retort, thus:—

$$\begin{matrix} C_2H_3O \\ C_7H_5O \end{matrix} O + \begin{matrix} C_2H_3O \\ C_7H_5O \end{matrix} O = \begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix} O + \begin{matrix} C_7H_5O \\ C_7H_5O \end{matrix} O.$$

We may just mention that it was in this way, *i. e.*, by the decomposition of the benzoic acetate, that Gerhardt first prepared the acetic anhydride.*

395. Alcohols and the so-called hydrated acids, ethers, and acid anhydrides, are bodies of the same kind. Philosophically, alcohols, acids, salts, ethers, and acid anhydrides, may be reduced to the same generic formula,—to the formula of water, in which one or two atoms of hydrogen are replaced, either by simple metals, or by hydrocarburetted groups (methyl, ethyl, phenyl, &c.), or else by oxygenated groups (othyl, benzoyl, cuminyl, &c.) The relation may be carried still further. We have ethyl, methyl, &c., and their hydrides, which may be referred to the formula of hydrogen, thus:—

Molecule of Hydrogen.	Molecule of ethyl.	Molecule of hydride of ethyl.
H, H	C_2H_5, C_2H_5	C_2H_5, H.

Even if we reject that view of the constitution of aldehyde which would make it the hydride of othyl, we have the chloride of othyl, which is to othyl what hydride of ethyl is to ethyl, with the exception of having chlorine in the place of hydrogen; and Gerhardt obtained, in distilling benzoic salicylate, benzoyl, $Bz, Bz = \begin{matrix} C_7H_5O \\ C_7H_5O \end{matrix}$; that is to say, it is to hydrogen, H H, what hydrated benzoic acid and benzoic anhydride are to water. We shall contrast certain organic compounds belonging to the type water, and certain others belonging to the type hydrogen. The student will at once see the analogy which exists between them.

$\left.\begin{matrix} H \\ H \end{matrix}\right\}$ free hydrogen. $\left.\begin{matrix} H \\ H \end{matrix}\right\}$ O, water.

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* We recommend the student to consult two papers by the late lamented M. C. Gerhardt, in vol. v. of the *Chemical Society's Journal*, on the "Constitution of Organic Acids."

$\left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\}$	hydride of ethyl.	$\left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\}$	O, alcohol.
$\left.\begin{matrix} C_2H_3O \\ H \end{matrix}\right\}$	aldehyde.	$\left.\begin{matrix} C_2H_3O \\ H \end{matrix}\right\}$	O, acetic acid.
$\left.\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\right\}$	acetyl, still to be discovered.	$\left.\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\right\}$	O, acetic anhydride.
$\left.\begin{matrix} C_2H_3O \\ CH_3 \end{matrix}\right\}$	acetone.	$\left.\begin{matrix} C^3H_3O \\ CH_3 \end{matrix}\right\}$	O, acetate of methyl.

396. *The different views which have been and are held on the constitution of ammonia.*—We must now make the student acquainted with the views which have been and are held on the constitution of ammonia and its derivatives. The first we shall notice is that proposed by Sir Robert Kane, which regarded NH_2 (amidogen) as the radical of ammonia. The author of the amidogen theory thus describes his views in his "Elements of Chemistry:"—"The real nature of ammonia has recently been the subject of much inquiry. Its equivalent is satisfactorily determined to be 17, and hence its formula is NH_3, and its equivalent volume 4. It may enter into combination directly with dry oxygen acids, but it does not then form the proper ammoniacal salts, which all contain an atom of water essential to their constitution. It combines with a great number of saline bodies, and then resembles in its functions their water of crystallization. Its most remarkable property, however, is, that in acting on metallic compounds, and on certain organic acids, it abandons an atom of hydrogen, and the remaining NH_2 combines with the metal, or with the radical of the acid. Thus, with $HgCl$, and NH_3, there results $HgNH_2$ and HCl; with $PtCl_2$, and $2NH_3$, there are formed $Pt + NH_2$ and $2HCl$. Of organic bodies, oxalate of ammonia gives, when heated, $C_2O_2 + NH_2$; and benzoate of ammonia produces, similarly, $C_{14}H_5O_2 + NH_2$. It is hence evident that the third atom of hydrogen is not so intimately combined with the nitrogen as the remaining two. It may be eliminated by the simplest reactions; but the N and H_2 remain much more firmly united, and separate only when the constitution of the ammonia is totally broken up. I hence concluded that the NH_2 should be considered as the radical of ammonia, and proposed to term it *amidogene*, and its symbol Ad. The ammonia is then *amidide of hydrogen*, and its rational

formula, NH_2, H, or Ad, H. Ammonia is thus assimilated to water, and to chloride of hydrogen, in constitution; the radical amidogene having the closest analogy to oxygen and chlorine. These conclusions have been almost unanimously adopted by chemists.

397. "These views are remarkably illustrated by the action of ammonia on potassium. When this metal is heated in the dry gas, hydrogen is disengaged, and a fusible olive-green substance is obtained. The quantity of hydrogen evolved is the same as that which the metal should evolve from water, that is, one atom; and the olive body consists of K, NH_2. It is *amidide of potassium*. When put into water, potash and ammonia are produced, K, Ad and HO giving KO, and H, Ad. When this olive substance is heated nearly to redness, ammonia is expelled, and *nitruret of potassium* remains, $3(K, NH_2)$, giving $2NH_3$ and K_3N. The phenomena are exactly the same with sodium; an amidide and a nitruret of sodium being thus formed." Amidogen has never been isolated.

398. As ammoniacal salts strongly resemble in their character the salts of potassium and sodium, and as the ammoniacal compound which replaces potash or soda is not NH_3, but $NH_3 + HO$, Berzelius considered that the ammoniacal compound which exists in the haloid salts of ammonia, is a hypothetical substance ammonium, NH_4, which is capable of playing the part of a metal, and which is isomorphous, as we have already seen, with potassium and sodium. Berzelius also considers it is the oxide of this hypothetical body, ammonium, which exists in the oxygen salts of ammonia; and it is also formed, he supposes, when the gas, NH_3, is dissolved in water, the NH_3 uniting with one atom of HO, forming NH_4O.

399. The theory of ammonium is supposed to derive considerable support from the following experiments:—"When a globule of mercury is placed on a piece of moistened caustic potash, and connected with the negative side of a voltaic battery of very moderate power, while the circuit is completed through the platinum plate upon which the alkali rests, decomposition of the latter takes place, and an amalgam of potassium is rapidly formed.

400. "If this experiment be now repeated with a piece of chloride of ammonium, instead of hydrate of potash

a soft, solid, metalline mass is also produced, which has been called the *ammoniacal amalgam*, and considered to contain ammonium in combination with mercury. A still simpler method of preparing this extraordinary compound is the following:—A little mercury is put into a test-tube, with a grain or two of potassium or sodium, and a gentle heat applied; combination ensues, attended by heat and light. When cold, the fluid amalgam is put into a capsule, and covered with a strong solution of chloride of ammonium. The production of an ammoniacal amalgam instantly commences; the mercury increases prodigiously in volume, and becomes quite pasty. The increase of weight is, however, quite trifling; it varies from $\frac{1}{1800}$ to $\frac{1}{12000}$ part.

401. "Left to itself, the amalgam quickly decomposes into fluid mercury, ammonia, and hydrogen."

402. It is difficult to offer any opinion concerning the real nature of this compound. Something analogous occurs when pure silver is exposed to a very high temperature, much above its melting point, in contact with air, or oxygen gas. The latter is absorbed in very large quantity, amounting, according to the observation of Gay Lussac, to twenty times the volume of the silver, and is again disengaged on lessening the heat. The metal loses none of its lustre, and is not sensibly altered in other respects.

403. "The great argument in favour of the existence of ammonium is founded on the perfect comparison which the ammoniacal salts bear with those of the alkaline metals."

404. We must not neglect to point out to the student that the anhydrides of some of the dibasic acids and NH_3 can unite together. If the anhydride is in excess, an amidated acid is formed; but if the ammonium is in excess, compounds are formed which are considered to be the ammonium salts of these acids. Both these classes are, according to the new views, constructed on the water type. We give the formula, both on the old and new view, employing, in the former case, the old atomic weights of sulphur and oxygen; in the latter, the new:—

	Old view.	New view.
Sulphamic acid - -	$2NH_3, SO_3$	$\left.\begin{matrix}NH_2(SO_2)'' \\ H\end{matrix}\right\}O$

	Old view.	New view.
Sulphamate of ammonium	NH_3, SO_3	$\left.\begin{matrix}NH_2(SO_2)'\\NH_4\end{matrix}\right\}O$
Thionamic acid - -	$2NH_3, SO_2$	$\left.\begin{matrix}NH_2(SO)'\\H\end{matrix}\right\}O$
Thionamate of ammonium	NH_3, SO_2	$\left.\begin{matrix}NH_2(SO)'\\NH_4\end{matrix}\right\}O$
Carbamic acid - -	$2NH_3, CO_2$	$\left.\begin{matrix}NH_2(CO)'\\H\end{matrix}\right\}O$
Carbamate of ammonium	NH_3, CO_2	$\left.\begin{matrix}NH_2(CO)'\\NH_4\end{matrix}\right\}O$

These amidogen acids differ from their acid salts of ammonium by one atom of water; they can be formed by the action of heat on these ammoniacal salts, an atom of water being eliminated. Thus:—

Acid oxalate of ammonium. Oxamic acid.

$$\left.\begin{matrix}(C_2O_2)''\\H(NH_4)\end{matrix}\right\}O_2 - \left.\begin{matrix}H\\H\end{matrix}\right\}O = \left.\begin{matrix}NH_2(C_2O_2)\\H\end{matrix}\right\}O$$

405. It will be less perplexing to the student if we explain subsequently the meaning of the terms *amide* (although the term amide has, to a certain extent, been already explained), *nitride*, and *imide*.

406. The nitrogen compounds of the metals which Sir Robert Kane viewed as containing a radical amidogen, united with a metal, M. Laurent views as ammonias in which one or more of the equivalents of hydrogen are replaced by a corresponding number of the equivalents of the metal. This view of Laurent's, we shall see hereafter, has been singularly confirmed. In order that the student may distinctly understand the constitution of bodies, according to both theories, we append a few examples, formulated according to both views:—

KANE.	LAURENT.
Chloroamidide of mercury.	Chloride of dimercuriammonium.
$HgCl, HgAd$	$Hg_2H_2NCl.$
Subchloride and subamide of mercury.	
$Hg_2Cl + Hg_2Ad$	$HgH_2NCl + Hg_2Cl$
PtO_2, Ad_2H_2	$PtH_2NO, HO.$*

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* We shall see, presently, that there are two classes of ammoniacal bodies. One class is called *amines*, the other *amides*. From their totally

407. The general term, *metalamine*, is given to those compounds which are on the oxide of ammonium type, and which are basic in their character; whilst the bodies which are on the type of $N\,H_3$, and which are neutral in their character, are termed *metalamides*.

408. Our outline of the different views which have been and are held on the constitution of the ammoniacal bodies, would be incomplete, if we did not notice the different views which have prevailed as regards the constitution of the *alkaloids*, or *organic alkalies*, or *organic bases*, as they are indifferently called. They all contain nitrogen; they possess, for the most part, decided basic properties. When dissolved, they act on vegetable colours like the inorganic alkalies; they combine, like ammonia, with the hydrogen acids, and with the hydrated oxygen acids, forming salts, which are generally crystallizable. Their chlorides, like chloride of ammonium, form double salts with bichloride of platinum, terchloride of gold, and with chloride of mercury. Most of them, at the ordinary temperature, are expelled from their salts by ammonia, but many of them, at the temperature of boiling water, expel ammonia from its salts, on account of the greater volatility of ammonia. Some of them contain oxygen as a constituent; others of them do not. The basic properties of those that do contain oxygen cannot be owing to the presence of that element, as no variation in its amount affects their neutralizing power. They evidently derive their distinctive features, as a class, from the nitrogen they contain, and the form in which the other constituents are associated with it. There is a very strong similarity between these bodies and ammonia; there is, therefore, evidently a relation between them. Different views have been taken of the nature of this relation. Berzelius considered that they contained ammonia ready formed, and it was this body which conferred upon them their basic character, and to the ammonia was joined in their constitution different neutral principles, which, for the most part, were not susceptible of isolation. According to this view, the formulæ of quinine and morphine would be,—

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different behaviour with the alkalies (415), it would appear that the amines are constituted in the way Laurent suggests; whilst the amides are probably constituted in the way Sir Robert Kane suggests.

Quinine - - $C_{20} H_{24} N_2 O_2 = C_{20} H_{21} N O_2, N H_3$
Morphine - $C_{19} H_{19} N O_3 = C_{17} H_{16} O_3, \quad N H_3$

This view derives some support from the fact that ammonia can unite with a limited class of neutral substances, such as oil of mustard, and oil of bitter almonds; and that the compounds produced by this union are basic bodies, which resemble, in properties and composition, several of the organic bases produced. The recent researches of Hofmann and others, on the organic bases, prove that the majority of these bodies are not constituted in the way Berzelius supposed; and even those that appear at present to be so constituted, will, very probably, be found hereafter to be constituted on the general rather than on a particular type. The student must also bear in mind what has been stated on the proximate constitution of bodies, and he will see that though ammonia and a neutral principle may produce a basic body by uniting together, it does not follow that these substances *exist* in the substance which has been formed by their union.

409. As no ammonia could be detected in these bodies, Liebig, several years ago, suggested a different view of their constitution. He considered that they might be derivatives of ammonia ($N H_3$), in which an equivalent of hydrogen has been displaced by an equivalent of an organic group; *he even predicted*, that if it should be found possible to displace this equivalent of hydrogen by ethyl, or by some electro-positive hydrocarbon, a powerful volatile base would probably be obtained. We will formulate the organic base, aniline, according to the views both of Berzelius and Liebig, in order that the student may clearly perceive the difference between the two theories:—

Berzelius.	Liebig.
$C_6 H_4, N H_3$	$\left.\begin{matrix} C_6 H_5 \\ H \\ H \end{matrix}\right\} N$

410. Subsequently, Wurtz realized Liebig's prediction; he obtained three organic alkalies, all volatile, like ammonia, and all possessing a strong, pungent, ammoniacal smell; they are constituted in the following way,—they are ammonias, in which one atom of the hydrogen has been

displaced in one by methyl ($C\,H_3$), in the second by ethyl ($C_2\,H_5$), and in the third by amyl ($C_5\,H_{11}$). Wurtz obtained them by the action of potash on cyanate of methyl, cyanate of ethyl, and cyanate of amyl. We will now exhibit these reactions, and also the action of potash on cyanic acid, as the latter reaction will prove to the student that the alkaline bodies produced by Wurtz must be constructed on the same type as ammonia.

Cyanic acid. Carbonate of potassium.

$$\left.\begin{matrix}C\,N\\H\end{matrix}\right\}O + 2\left.\begin{matrix}K\\H\end{matrix}\right\}O = \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N + \left.\begin{matrix}C\,O'\\K_2\end{matrix}\right\}O_2$$

Cyanate of methyl. Methylamine.

$$\left.\begin{matrix}C\,N\\C\,H_3\end{matrix}\right\}O + 2\left.\begin{matrix}K\\H\end{matrix}\right\}O = \left.\begin{matrix}C\,H_3\\H\\H\end{matrix}\right\}N + \left.\begin{matrix}C\,O'\\K_2\end{matrix}\right\}O_2$$

Cyanate of ethyl. Ethylamine.

$$\left.\begin{matrix}C\,N\\C_2\,H_5\end{matrix}\right\}O + 2\left.\begin{matrix}K\\H\end{matrix}\right\}O = \left.\begin{matrix}C_2\,H_5\\H\\H\end{matrix}\right\}N + \left.\begin{matrix}C\,O'\\K_2\end{matrix}\right\}O_2$$

Cyanate of amyl. Amylamine.

$$\left.\begin{matrix}C\,N\\C_5\,H_{11}\end{matrix}\right\}O + 2\left.\begin{matrix}K\\H\end{matrix}\right\}O = \left.\begin{matrix}C_5\,H_{11}\\H\\H\end{matrix}\right\}N + \left.\begin{matrix}C\,O'\\K_2\end{matrix}\right\}O_2$$

411. Wurtz also obtained them from the cyanuric ethers, and from the ureas.

412. We have seen that Liebig considered that the organic alkalies might be ammonia in which one of the three atoms of hydrogen had been replaced by an electro-positive hydro-carbon like ethyl; that Wurtz realized this idea by obtaining three organic alkalies, in which one of the hydrogen atoms of ammonia was actually replaced by an electro-positive body; but it was reserved for Hofmann to conceive the beautiful, and what he has also proved by his elaborate researches to be a truthful, idea —that not only one but even two or three atoms of hydrogen might be replaced by organic bodies; that two equivalents of the hydrogen might be replaced by two

equivalents of one *monatomic* radical, or by two different monatomic radicals; all the three equivalents of hydrogen might be replaced by three equivalents of the same monatomic radical, or two equivalents by one, and one equivalent by another; or by three different monatomic radicals. But he has also proved that, under the influence of agents apt to replace more or less hydrogen, two, three, four, and probably even five, atoms of ammonia are capable of coalescing into atoms of a higher order, in which two, three, twelve, or perhaps even fifteen of the hydrogen atoms can be replaced in equivalent proportions by other bodies. But he has even gone further, for he has formed bodies corresponding to the nitrogen ammonias, but having, in the place of the nitrogen, phosphorus, arsenic, or antimony. Dr. Hofmann has even gone further still; he has shown that, under special circumstances, ammonia has the power of associating with its phosphuretted, arsenetted, and antimonetted analogues, so as to form molecules of a higher order, containing simultaneously nitrogen and phosphorus, nitrogen and arsenic, nitrogen and antimony, perhaps even three or four of these elements.

413. "The derivatives of ammonia may be at once subdivided into two large groups, namely,—

"A. Bodies in which the chemical character of ammonia is preserved; and,—

"B. Bodies in which the chemical character of ammonia has become extinct.

414. "The group A embraces that large number of compounds known as organic bases, many of which are elaborated in animals and plants (animal and vegetal alkaloids), whilst the greater number are produced in the laboratory (artificial bases). This group is often designated by the general term amines, which may again be subdivided into monamines, diamines, triamines, tetramines, &c., according as they are derived from one, two, three, or four atoms of ammonia. The second group, B, consists of neutral bodies, mostly produced by artificial processes, comparatively few terms of this group having been met with in the animal or vegetal organism. They are distinguished by the general designation amides, and may be similarly subdivided into monamides, diamides, triamides, tetramides, &c.

A. Amines.	B. Amides.
a. Monamines.	*a. Monamides.*
b. Diamines.	*b. Diamides.*
c. Triamines.	*c. Triamides.*
d. Tetramines.	*d. Tetramides.*

415. "The most characteristic mark of distinction between the amines and amides is furnished in the deportment of the two classes under the influence of decomposing agents. Hitherto very few processes are known in which the amines yield up, in any form, the radicals whose introduction into ammonia has produced them. The amides, on the other hand, are readily decomposed into ammonia and the hydrated oxides of their radicals. The simplest manner of distinguishing an amine from an amide consists in boiling the compound under examination with potash, when the amine remains unaltered, the amide evolving ammonia, with the formation of a potassium salt.

416. "This classification into amines and amides, although far from embracing every individual member of the host of ammonia-derivatives, either known or conceivable, serves as a thread to guide one through the intricacies of this numerous class of compounds." *

417. But Hofmann has even gone further still. He has proved, by *analogy*, that a solution of ammonia in water is, as Berzelius supposed, a solution of the hydrate of the oxide of the compound radical ammonium, $N H_4$, just as in soda and potash solutions there exist the hydrates of sodium and potassium. We say that Hofmann has proved this by analogy; the proof is this:—He has replaced the last equivalent of ammonium hydrogen by a compound radical. He has obtained, for example, a body which he has designated the hydrated oxide of tetrethyl-ammonium, in which the four atoms of hydrogen in ammonium are replaced by four atoms of ethyl.

418. Having given the history of the origin of types, we must now show how Gerhardt developed and generalized these ideas, and formed them into one harmonious group. In doing so, we shall have to return to some subjects we have already pretty fully explained.

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* Dr. Hofmann, "On Ammonia and its Derivatives," in Vols. XI. and XII. of the *Quarterly Journal of the Chemical Society.*

419. *Double decomposition regarded as the type of chemical action in general.*—Double decomposition is an action taking place between two compound atoms (two binary compounds); all chemical changes must be regarded as double decompositions, if we admit that the atoms of the elements and compound radicals, in their free state, are united in *pairs;*[*] if we do not admit that the atoms of these bodies are united in pairs, then all chemical changes are divided into three classes, viz., combination, single decomposition, and double decomposition. We give examples of the different classes, on the old view, and we also give them according to the new view, in which we assume that the atoms of the elements and compound radicals, in their free state, exist in *pairs.* All these decompositions become reduced, on this assumption, to one type, that of double decomposition, as the student will see by the examples.

OLD VIEW.		NEW VIEW.
I. $H + I = HI$	(combination)	I. $HH + II = HI + HI$
II. $HI + Zn = ZnI + H$	(decomposition)	II. *a.* $HI + ZnZn = ZnI + ZnH$
III. $HI + HgCl = HgI + HCl$	(double decomposition)	*b.* $HI + ZnH = ZnI + HH$
		III. $HI + HgCl = HCl + HgI$

420. *The meaning of formulæ.* — Chemical formulæ, according to the new views, do not represent the arrangement of the atoms in a compound, they are only for rendering evident, in the most simple and exact manner, the relations by which the bodies are connected when under the influence of transformations. Every transformation, every chemical reaction, can be rendered evident by giving in an equation the reacting materials, and the products of reaction. To represent a body by a *rational formula,* is to sum up by conventional signs a certain number of equations in which this body figures, some other body being taken as the unit of comparison. Rational formulæ are, therefore, in a certain sense, contracted equations.

421. We have already stated (178) that the rational formula of a chemical substance is but a memorandum of

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[*] We shall point out, in the next chapter, what we consider to be exceptions to the theory that the atoms of bodies in their free state are united in pairs, for we shall show that in such cases the molecular and chemical atoms are the same.

its reactions, and a particular mode of expressing the law of the synthesis and analysis of the body, apart from which it has but little meaning. A rational formula is, therefore, not an expression of the constitution of a body in a state of rest, but it is deduced from the modes of formation and decomposition of the body. Viewing rational formulæ in this light, we can see why $Ba\,O, S\,O_3$ should be preferred to the other formulæ which might be deduced from the modes of formation and decomposition of this body, sulphate of baryta. $Ba\,O, S\,O_3$ has the advantage of the other formulæ which might be deduced for sulphate of baryta from some of its reactions, because it recalls to our recollection a certain number of analogies of a certain number of bodies which it is made to resemble; and, in particular, those double decompositions of which sulphate of baryta is susceptible, in imitation of other sulphates, or of other salts of baryta. When we represent sulphate of baryta as a combination of an acid and a base, it is less for expressing the mode of formation of this salt by the direct union of the acid and the base, than for showing its resemblance, under the influence of chemical transformations, to sulphate of lead or sulphate of iron, to phosphate of baryta or nitrate of baryta. We wish thus to show that we can, in sulphate of baryta, replace the oxide of barium by oxide of lead, or oxide of iron, and thus transform it into other sulphates; or that we can replace the sulphuric acid by phosphoric acid or nitric acid, and thus transform it into other salts of baryta. In a word, the formula which makes sulphate of baryta a kind of double edifice, composed of an acid and a base, shows that we can convert this body by double decomposition into a certain number of analogous compounds. To take another illustration—we can form alcohol by uniting olefiant gas and water; we can also decompose alcohol into olefiant gas and water. On the other hand, we cannot decompose alcohol into ethyl, $C_4\,H_5$, and water, or form alcohol by uniting ethyl and water; yet we attribute to alcohol a formula $C_4\,H_5, H\,O$, which in a certain sense implies that it contains ethyl. Now, why do we accord this formula to alcohol rather than $C_4\,H_4, H_2\,O$? Because in the great majority of double decompositions, in which alcohol is one of the reacting substances, the radical or residue, $C_4\,H_5$, is transferred from the alcohol to some other substance in exchange for hydrogen, or one of its representatives. Examples:—When alcohol is treated with potassium, one-sixth of the hydrogen is evolved, and the compound C_2H_5, KO is formed. Again, when alcohol is treated with chloride, bromide, or iodide of phosphorus, it yields the compound C_2H_5Cl, or C_2H_5Br, or C_2H_5I; and when the compound C_2H_5, KO is treated with C_2H_5I, ether and iodide of potassium are formed, as we have already seen. There is no proof that the C_2H_5 exists preformed in alcohol; the formula, which is but a contracted equation, is simply intended to express the fact that C_2H_5 is the group of atoms which alcohol most frequently exchanges for other bodies in double decompositions.

422. *The same body can have more than one rational formula.*—Either the definition we have given of a rational formula is incorrect, or some bodies, at least, must have more than one rational formula; for if a rational formula expresses the mode of formation and decomposition of a substance—in other words, is but a contracted equation—then, as sulphate of baryta can be formed from, and decomposed into, other substances besides BaO and SO_3, and as alcohol can be formed from, and be decomposed into, olefiant gas and water, these substances must have other formulæ besides BaO, SO_3 and C_2H_5, HO.

423. Formulæ, according to the old view, represent (what is considered to be) the mode of arrangement of the atoms in a compound. According to this view, there can be but one formula for a body, as its atoms must always be arranged in the same way. Formulæ, according to the new view, do not represent bodies in a state of rest, but in a state of motion; they represent the manner in which the atoms of the bodies are supposed to arrange themselves when subjected to certain influences. It is evident that if a compound is composed of but two or three simple atoms, they can have, even according to this view, but one arrangement, and, therefore, the body can have but one rational formula. But when the number of atoms in a compound is more numerous, one formula cannot express all the possible arrangements of the atoms, or all the analogies; the number of rational formulæ will, therefore, depend upon the complexity of the body, for, with the increase in the atoms of a compound, the possible arrangement of the atoms in double decomposition will increase,

and, therefore, the number of rational formulæ which may be assigned to the body will likewise increase. We shall now give some examples to illustrate the fact that when the same substance is brought into contact with different agents, each of which is capable of making it undergo double decomposition, it often happens that it does not present to each re-agent the same side for attack; in other words, it does not exchange with each of the re-agents the same group of elements (the same radical or residue). Such a substance can therefore be represented by several rational formulæ.

EXAMPLES.*

1. Oil of bitter almonds behaves in many re-actions as the hydride of the radical benzoyl.

$$H, C_7H_5O.$$

This formula shows the same relation between oil of bitter almonds and benzoic acid (oxide of benzoyl) as exists between hydrogen gas and water, or the same relation between the oil and chloride of benzoyl, Cl, C_7H_5O, as exists between hydrogen and hydrochloric acid. It corresponds in the following reactions:—(1) The action of air converts the oil into benzoic acid; (2) chlorine transforms the oil into chloride of benzoyl; (3) the hydride of copper and chloride of benzoyl produce the oil:—

2 Atoms of the oil of bitter almonds. — Acid benzoric anhydride.

$$(1)\quad H_2 \left\{ \begin{matrix} C_7H_5O \\ C_7H_5O \end{matrix} \right. + OO = O \left\{ \begin{matrix} C_7H_5O \\ C_7H_5O \end{matrix} \right. + H_2O.$$

Oil of bitter almonds. — Chloride of benzoyl.

$$(2)\quad H, C_7H_5O + Cl\,Cl = Cl, C_7H_5O + H\,Cl.$$

$$(3)\quad Cl, C_7H_5O + Cu_2H = H, C_7H_5O + Cu_2Cl.$$

But in other cases, the double decomposition, instead of being effected upon one atom of the hydrogen of the oil, is effected upon the oxygen of the body; the oil then comports itself as an oxide, and not as a hydride. Such is the action of ammonia (4), of aniline (5), &c., upon the oil.

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* In future, the new atomic numbers will be employed, unless the contrary is stated.

2 Atoms of ammonia. 3 Atoms of the oil of bitter almonds. Hydrobenzamide. 3 Atoms of water.

$$(4)\quad N_2 \left\{ \begin{matrix} H_3 \\ H_3 \end{matrix} \right. + 3\,O \left\{ \begin{matrix} C_7H_5 \\ H \end{matrix} \right. = N_2 \left\{ \begin{matrix} (C_7H_5)_3 \\ H_3 \end{matrix} \right. + 3\,O \left\{ \begin{matrix} H \\ H \end{matrix} \right.$$

Aniline. Oil of bitter almonds. Benzoylanilide.

$$(5)\quad N \left\{ \begin{matrix} C_6H_5 \\ H \\ H \end{matrix} \right. + O \left\{ \begin{matrix} C_7H_5 \\ H \end{matrix} \right. = N \left\{ \begin{matrix} C_6H_5 \\ C_7H_5 \\ H \end{matrix} \right. + O \left\{ \begin{matrix} H \\ H \end{matrix} \right.$$

The more complicated a body is in its composition, the more numerous obviously are the points of attack which it will offer to chemical agents; such a body will, therefore, have many rational formulæ; in virtue of this principle, the oil of bitter almonds is therefore represented at times as the hydride of the radical C_7H_5O, and at times as the oxide of the radical C_7H_5.

2. Cyanic acid, the metallic cyanates, the cyanic ethers, are the oxides of the monatomic radical cyanogen; the sulphocyanic acid is a sulphide of the same radical.

Cyanic acid, or oxide of cyanogen and hydrogen	$CHNO = O \left\{ \begin{matrix} Cy \\ H \end{matrix} \right.$
Metallic cyanates, or oxides of cyanogen and metal	$CMNO = O \left\{ \begin{matrix} Cy \\ M \end{matrix} \right.$
Cyanic ether, or oxide of cyanogen and ethyl	$C(C_2H_5)NO = O \left\{ \begin{matrix} Cy \\ C_2H_5 \end{matrix} \right.$
Sulphocyanic acid, or sulphide of cyanogen and hydrogen	$CHNS = S \left\{ \begin{matrix} Cy \\ H \end{matrix} \right.$

These rational formulæ signify that in double decompositions the bodies for which their formulæ stand, exchange cyanogen for another radical; or that they are formed from like double decompositions. Cyanic acid and sulphocyanic acid are, so to speak, to the body called chloride of cyanogen, that which water and sulphide of hydrogen are to hydrochloric acid.

But these cyanic compounds are formed from double decompositions; or they exchange in double decompositions not the radical CN, but the radical CO of the carbonic combinations. Thus, (1) cyanic acid and water, when brought together, undergo double decomposition, carbonic acid and ammonia being formed; (2) potash transforms cyanic ether into carbonic acid and ethylamine; (3) sulphocyanic acid is formed from the reaction of ammonia upon sulphide of carbon. It is, therefore, also rational to represent and speak of these cyanic compounds as the nitrides of the biatomics radical carbonyle CO, and sulphocarbonyle CS.

Cyanic acid, or the nitride of carbonyle and hydrogen -	$CHNO = N\left\{\begin{matrix}CO\\H\end{matrix}\right.$
Metallic cyanates, or nitrides of carbonyle and metal -	$CMNO = N\left\{\begin{matrix}CO\\M\end{matrix}\right.$
Cyanic ether, or nitride of carbonyle and ether -	$C(C_2H_5)NO = N\left\{\begin{matrix}CO\\C_2H_5\end{matrix}\right.$
Sulphocyanic acid, or nitride of sulphocarbonyle and hydrogen - - -	$CHNS = N\left\{\begin{matrix}CS\\H\end{matrix}\right.$

These formulæ express, for example, that cyanic acid is to ammonia that which carbonic acid is to water, &c. These double decompositions, from which the cyanic combinations *are formed* by the metamorphosis of carbonic combinations, or which *give* carbonic combinations by the metamorphosis of the cyanic compounds, can therefore be thus expressed:—

$$\text{(1)}\quad \overset{\text{Cyanic acid.}}{N\left\{\begin{matrix}CO\\H\end{matrix}\right.} + O\left\{\begin{matrix}H\\H\end{matrix}\right. = N\left\{\begin{matrix}H\\H\\H\end{matrix}\right. + \overset{\text{Carbonic acid.}}{O, CO}$$

$$\text{(2)}\quad \overset{\text{Cyanic ether.}}{N\left\{\begin{matrix}CO\\C_2H_5\end{matrix}\right.}\quad \overset{\text{2 Atoms of hydrate of potash.}}{O_2\left\{\begin{matrix}H_2\\K_2\end{matrix}\right.} = \overset{\text{Ethylamine.}}{N\left\{\begin{matrix}H\\H\\C_2H_5\end{matrix}\right.} + \overset{\text{Carbonate of potassium.}}{O_2\left\{\begin{matrix}CO\\K_2\end{matrix}\right.}$$

$$\text{(3)}\quad N\left\{\begin{matrix}H\\H\\H\end{matrix}\right. + \overset{\text{Sulphide of carbon.}}{SCS} = \overset{\text{Sulphocyanic acid.}}{N\left\{\begin{matrix}CS\\H\end{matrix}\right.} + \overset{\text{Sulphide of hydrogen.}}{S\left\{\begin{matrix}H\\H\end{matrix}\right.}$$

424. One formula cannot, therefore, represent all the decompositions and recompositions of a complex body;

its most general formula—the one by which it will most usually be represented—will therefore be that by which the greatest number of its formations and transformations can be explained. But, although a complex body may have many formulæ, practically, however, it is found that a small number of rational formulæ, seldom more than two or three, suffices for each compound; and, moreover, that the formulæ of all bodies whatever, may be reduced to a small number of general types.

425. This idea of Gerhardt's, that a body may have several rational formulæ, is capable of explaining the apparent contradictions which have existed in organic chemistry. Hitherto, one chemist having studied one set of decompositions and recompositions of a body, deduced from these chemical changes a formula for it; another chemist having studied another set of formations and transformations of the same body, deduced another formula: each, of course, gained a certain number of adherents for his view of its constitution. These contradictory, and sometimes hostile interpretations, rendered organic chemistry a chaos to the student. But Gerhardt's view reconciles these conflicting interpretations; each may be right, as the body may have more than one formula. Order and harmony are therefore restored, and doubt, and its attendant difficulties, cease to beset the student's path. But it does even more than this; it opens up to students a glorious prospect in the field of organic research. For the student will readily perceive, from this view of chemical formulæ, how much more numerous and interesting must be the discoveries in organic, over those in inorganic chemistry, on account of organic bodies having in general a much greater complexity of composition, and, therefore, susceptible of more numerous formations and transformations.

426. *Molecular types.*—"In considering the composition and the properties of chemical compounds, both mineral and organic, it is found that they may be referred to a comparatively small number of substances, of extremely simple constitutions, from which they may be supposed to arise by substitution." The substances from which the others are supposed to arise by substitution are, therefore, the *patterns* or *types* upon which the other bodies are founded. Bodies belonging to the same type must be

analogous in constitution and yield analogous reactions. Gerhardt adopts four types, viz.:—

Water, $\left.\begin{matrix}H\\H\end{matrix}\right\}O$, from which are derived the oxides, sulphides, selenides, and tellurides.

Hydrochloric acid $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$ the type of the chlorides, bromides, iodides, fluorides, and cyanides.

Ammonia, $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$, the type of the nitrides, phosphides, arsenides, &c.

Hydrogen, $\begin{matrix}H\\H\end{matrix}$ $\Big\{$ the type of the elementary bodies, compound radicals, hydrides of metals, and radicals, &c.

427. These typical formulæ all correspond to two volumes of vapour.

428. There are, however, a great many substances which do not admit of being ranged under the above types, unless we make the additional assumption that, under particular circumstances, two, three, or even more molecules of hydrogen, of hydrochloric acid, of water, or of ammonia, may be condensed into new molecules, which, notwithstanding the accumulation of matter in them, still *occupy*, in the state of vapour, the *same space* which we have recognised as characteristic of the original molecules, viz., two volumes. This condensation takes place under the influence of groups of elements which are capable of replacing more than one atom of hydrogen.

429. In iodide of ethyl, C_2H_5I, the group C_2H_5 is united with one atom of iodine; and since this substance exhibits, in many respects, the character of hydriodic acid, we refer it to the hydrochloric acid type. When this substance acts under favorable circumstances upon water, 1 or 2 atoms of hydrogen in the molecule of the water are replaced by ethyl, ethylic alcohol or ethylic ether being formed, with elimination of 1 or 2 molecules of hydriodic acid.

$$(1)\quad \left.\begin{matrix}H\\H\end{matrix}\right\}O + (C_2H_5)I = \left.\begin{matrix}(C_2H_5)\\H\end{matrix}\right\}O + HI.$$

$$(2)\quad \left.\begin{matrix}H\\H\end{matrix}\right\}O + 2\left\{(C_2H_5)I\right\} = \left.\begin{matrix}(C_2H_5)\\(C_2H_5)\end{matrix}\right\}O + 2HI.$$

430. The action of iodide of ethyl upon ammonia gives rise to the formation of three ethylated ammonias, which are formed by the substitution of ethyl for 1, 2, or 3 hydrogen-atoms in ammonia, thus:—

$$(1)\quad \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N + (C_2H_5)I \quad = \left.\begin{matrix}(C_2H_5)\\H\\H\end{matrix}\right\}N + HI.$$

$$(2)\quad \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N + 2\left\{\,(C_2H_5)I\right. = \left.\begin{matrix}(C_2H_5)\\(C_2H_5)\\H\end{matrix}\right\}N + 2HI.$$

$$(3)\quad \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N + 3\left\{\,(C_2H_5)I\right. = \left.\begin{matrix}(C_2H_5)\\(C_2H_5)\\(C_2H_5)\end{matrix}\right\}N + 3HI.$$

431. In hydriodic ether, in alcohol, in ether, and in the ethylated ammonias, the group C_2H_5 invariably replaces 1 atom of hydrogen, and, accordingly, a monatomic character is ascribed to ethyl.

432. On the other hand, the group C_2H_4, olefiant gas, or ethylene, is found to unite with two atoms of chlorine, bromine, and iodine, the compounds $(C_2H_4)Cl_2$, $(C_2H_4)Br_2$, and $(C_2H_4)I_2$ being formed. These substances imitate, in many respects, the deportment of iodide of ethyl, or hydriodic acid, and they may be assumed to have been formed from two molecules of hydrochloric, hydrobromic, or hydriodic acid; the two atoms of hydrogen being replaced by the group C_2H_4.

$$\text{2 molecules of hydrochloric acid - - }\left.\begin{matrix}H\\H\end{matrix}\right\}\begin{matrix}Cl\\Cl\end{matrix}\qquad (C_2H_4)\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\quad \text{Bichloride of ethylene.}$$

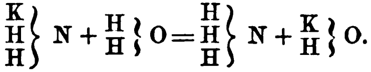
The two molecules of hydrochloric acid are held together by the insertion of the group C_2H_4 into the place of the two atoms of hydrogen; and during this insertion the volume of the two molecules of hydrochloric acid, which was originally $2 + 2 = 4$ volumes, has shrunk to ½, *i.e.*, to 2 volumes, the molecule $(C_2H_4)Cl_2$ occupying, in the state of vapour, a space not greater than that occupied by 1 molecule of hydrochloric acid. Groups of elements which are capable of replacing 2 atoms of hydrogen, and of linking, by such replacement, two molecules of a type, are called biatomic.

432. We have already noticed that bodies may be formed on the type of 2, 3, 4, or probably even 5 atoms

of ammonia; these polymolecules occupy, in the state of vapour, only the same space that one vapourized molecule occupies; this is the case likewise with bodies formed on the type of 2, 3, &c., atoms of H H, H Cl, and $\left.\begin{matrix}H\\H\end{matrix}\right\}O$; these complex molecules only occupy, in the state of vapour, the same space that one molecule occupies.

433. The different molecular types are persistent throughout that normal double decomposition which constitutes the most frequent case of chemical action. Two bodies belonging to the same, or, more frequently, to different types, react upon one another, with mutual interchange of certain of their constituents, to form new bodies belonging to the original types, thus:—

Potassamide.



$$\left.\begin{matrix}K\\H\\H\end{matrix}\right\}N+\left.\begin{matrix}H\\H\end{matrix}\right\}O=\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N+\left.\begin{matrix}K\\H\end{matrix}\right\}O.$$

434. We have seen that a body may have more than one formula, and its different formulæ may be constructed on different types; thus, as we have already noticed, cyanic acid and its congeners may be represented by two formulæ, $\left.\begin{matrix}Cy\\H\end{matrix}\right\}O$ and $\left.\begin{matrix}(CO)\\H\end{matrix}\right\}N$. The first of these two represents these compounds as formed on the water type, in which one atom of cyanogen has been substituted for an atom of hydrogen; the second formula is formed on the ammonia type, in which one atom of the biatomic radical carbonyl has been substituted for two atoms of hydrogen.

435. "By referring any complex body to a simple type, we pay regard only to such of its reactions, formative or transformative, as correspond with those of the type. But when more complex decompositions have to be expressed than the typical body is capable of undergoing, then the complex body can no longer be satisfactorily represented by its simple typical formula. Every compound body may, in fact, be represented by a series of typical formulæ, getting more and more complicated until they terminate in a mere synoptic expression of its constituent elements, which last constitutes, for every compound, its most general formula. Now, intermediate between

these ultimate expressions and those derived from our simple types, HCl, H_2O, and H_3N, we have formulæ derived from mixed chlorhydric acid-water, chlorhydric acid-ammonia, water-ammonia, and chlorhydric acid-water-ammonia types, thus:—

$$\begin{array}{l} HCl \\ \left.\begin{matrix} H \\ H \end{matrix}\right\} O \end{array} \qquad \begin{array}{l} HCl \\ \left.\begin{matrix} H \\ H \\ H \end{matrix}\right\} N \end{array} \qquad \begin{array}{l} \left.\begin{matrix} H \\ H \end{matrix}\right\} O \\ \left.\begin{matrix} H \\ H \\ H \end{matrix}\right\} N \end{array} \qquad \begin{array}{l} HCl \\ \left.\begin{matrix} H \\ H \end{matrix}\right\} O \\ \left.\begin{matrix} H \\ H \\ H \end{matrix}\right\} N \end{array}$$

436. "In these mixed types, multiples of some or all the constituent types may be substituted for the simple types above expressed.

437. "Benzamide furnishes us with a very good illustration of the use of formulæ derived from mixed types. It usually reacts as an ammonia, and consequently is usually represented on the ammonia type, to indicate the class of reactions of which it is susceptible. But it sometimes reacts as a hydrate, and we then represent it on the water type. But we may readily represent it also on the mixed water-ammonia type, whereby we not only indicate its capability of undergoing both sets of reactions, but we show at a glance the possibility of its being dehydrated into benzo-nitryl or cyanide of phenyl, C_7H_5N, thus:—

$$\left.\begin{matrix} (C_7H_5O)' \\ H \\ H \end{matrix}\right\} N \qquad \left.\begin{matrix} (C_7H_6N)' \\ H \end{matrix}\right\} O \qquad \begin{matrix} \left.H\right\} N \\ (C_7H_5)''' \\ \left.H\right\} O. \end{matrix}$$

Indeed, with the radical C_7H_5, a much greater variety of benzoic compounds and reactions can be expressed than is possible with the radicals C_7H_5O, or C_7H_6N. At the same time, for very many bodies, including benzamide $(C_7H_5O)H_2N$, the formulæ of Gerhardt, derived each from a simple primary type, are capable of expressing all the most familiar reactions of the bodies, and are best adapted to the general requirements of chemical science."*

438. *Equivalent values of radicals.*—A radical is *monatomic*, *biatomic*, *triatomic*, &c., according as its atom or

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* "Manual of Chemistry," by Dr. Odling.

molecule is capable of replacing, and is therefore equivalent to, one, two, three atoms, &c., of hydrogen. In alcohol and ether, for example,—

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O \qquad\qquad \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O.$$

The radical ethyl, C_2H_5, is *monatomic*, because it replaces one atom of hydrogen in the type, water; the radical sulphuryl, SO_2, is *biatomic*, because it can replace two atoms of hydrogen; Ex. $\left.\begin{matrix}(SO_2)''\\H_2\end{matrix}\right\}O_2$ sulphuric acid. The radical phosphoryl is *triatomic*, because it can replace three atoms of hydrogen; Ex. $\left.\begin{matrix}(PO)'''\\H_3\end{matrix}\right\}O_3$ phosphoric acid.*

439. We have seen that the same compound can have several rational formulæ; we have also seen that the different formulæ represent the body as containing different radicals; but to take one more example, nitric acid can be represented by the three following formulæ:—

$$\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}NO\\H\end{matrix}\right\}O_2 \qquad \left.\begin{matrix}N\\H\end{matrix}\right\}O_3.$$

440. In these three formulæ, the radicals NO_2, NO, and N, have three different equivalent values; NO_2 is the equivalent of one atom of hydrogen; NO is the equivalent of three atoms of hydrogen; N is the equivalent of five atoms of hydrogen, seeing that it is necessary to replace these three radicals by different quantities of hydrogen in order to form water:—

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}H_3\\H\end{matrix}\right\}O_2 \qquad \left.\begin{matrix}H_5\\H\end{matrix}\right\}O_3.$$

441. We can, therefore, according to the double decomposition we derive the formula from, change the radical in the same body; and the equivalent of the radical also becomes changed, after this law:—*Every equivalent of hydrogen which is added to a radical diminishes by unity the equivalent value of the entire radical; and every equivalent of hydrogen subtracted from a radical increases*

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* The halogen elements are monatomic; those forming the sulphur group are biatomic; those forming the nitrogen group are triatomic, and the silicon group tetratomic.

by unity the total equivalent value of the entire radical. For example, if we derive nitric acid from two atoms of water, N O is equivalent to three atoms of hydrogen, as seen in the notation,—

$$\left.\begin{matrix}N\,O\\H\end{matrix}\right\}O_2 \text{ equivalent of } \left.\begin{matrix}H_3\\H\end{matrix}\right\}O_2;$$

and when we wish, in order to express another analogy of the acid, to bring back the same formula to one atom of water, we commence by subtracting O, the equivalent of H_2, from one side of the formula, and adding it to the radical N O upon the other side, after the following manner:—

$$O + \left.\begin{matrix}N\,O\\H\end{matrix}\right\}O.$$

Now, by this transformation of two atoms of water into one atom, the four atoms of H, in the double atom of H_4O_2, are reduced to two atoms in the single atom of H_2O; and as the nitric acid contains an atom of hydrogen, it follows that the radical $N\,O + O = N\,O_2$ is equivalent to but one atom of H, that is to say, to H_3 (the equivalent of the radical N O) diminished by H_2, (which equivalent has been added to the radical N O): we have thus,—

$$\left.\begin{matrix}N\,O_2\\H\end{matrix}\right\}O \text{ equivalent of } \left.\begin{matrix}H\\H\end{matrix}\right\}O.$$

442. We learn, from the preceding examples, that the equivalents in hydrogen of radicals which correspond to different systems of double decomposition of the same body, bear to each other very simple proportions.

The equivalent of N O or N + O
is equal to $H_5 - H_2 = H_3$

The equivalent of $N\,O_2$ or NO + O
is equal to $H_3 - H_2 = H$.

443. These examples demonstrate that the equivalent in hydrogen of a radical composed of two other radicals, is equal to the difference of the equivalents of the two. This rule, which is general, we shall see is of great utility in the consideration of conjugate radicals.

444. When an element forms two or more oxides, capable of double decomposition, it has a different equi-

valent value in each. Thus, in the two oxides of mercury, Hg (= 100) has a different equivalent value in each. In the mercurious compounds it is semi-atomic, that is, it is equal to half an atom of hydrogen; therefore Hg_2 (= 200) is equal to one atom of H; but in the mercuric compounds, Hg (= 100) is equal to one atom of H; in other words, it is monatomic. In arsenious acid ($As_2\,O_3$). which is formed on the type of 3 atoms of water, As_2 is equivalent to H_6; and therefore As is equivalent to H_3; but in arsenic acid ($As_2\,O_5$), which is derived from 5 molecules of water, As is equivalent to H_5. In ferrous salts, Fe (= 28) is monatomic; in the ferric salts it is sesquiatomic, Fe_2 being equivalent to H_3.

445. Nitrogen, phosphorus, copper, platinum, bismuth, —in short, all the elements which are, like mercury, arsenic, and iron, capable of forming more than one oxide, have evidently more than one equivalent.

446. *Equivalent notation.*—Dashes are now added to symbols, to indicate the equivalent value of the substances for which the symbols stand. A semiatomic atom is indicated by two dashes to the left of the symbol, and placed below the line, thus, $_{\prime\prime}Hg$; a monatomic atom is indicated by a dash to the right of the symbol, and placed above the line, K'; a bi or di-atomic atom is indicated by two dashes to the right of the symbol, Sn''; a triatomic atom by three dashes to the right, Bi'''; a sesquiatomic atom is indicated thus, $Fe\,Fe''$, or Fe_2''.

447. *Conjugate radicals.*—For connecting two or more *systems* of double decomposition *of the same body*, it is frequently of advantage to represent these by a conjugate radical, that is to say, composed of two or more radicals, each of which recalls a like system. We can consider the radical of all bodies as conjugated which is capable, in certain reactions, of transforming itself into simple combinations appertaining to other radicals, or the radical of all bodies resulting from the metamorphosis of like combinations.

448. There are two ways of representing a conjugate radical; it can be conjugated either by *addition* or by *substitution*. It is conjugated by *addition* when it contains all the elements of two other simple or compound radicals. Thus, sulphophenyle, $C_6\,H_5\,(S\,O_2)$, is a radical conjugated by the addition of the radicals sulphuryle

$(S O_2)$, and phenyle $(C_6 H_5)$; stannethyle is a radical conjugated by the addition of the radicals stannicum (Sn') and ethyle $(C_2 H_5)$.

449. A radical is conjugated by *substitution* when it contains all the elements of one radical, and only a part of the elements of another radical,—the complete radical having replaced the absent elements of the imperfect radical. Thus, nitrobenzoyl, $C_7 H_4 (N O_2) O$, is composed of the radical benzoyl, in which one atom of hydrogen is replaced by the radical nitryle $(N O_2)$. Trichloracetyle, $C_2 (Cl_3) O$, is composed of the radical acetyle, $C_2 H_3 O$, in which 3 atoms of hydrogen are replaced by 3 equivalents of the radical chlorine.

450. The equivalent in hydrogen of a conjugate radical may be determined by the two following rules, deduced from the general law previously given (441):—

1st. *The equivalent in hydrogen of a radical conjugated by addition, is equal to the difference of the equivalents in hydrogen of the two radical constituents.*

EXAMPLES.

1. The conjugate radical cacodyle, $As''' (C H_3)'_2$, is equivalent to one atom of hydrogen.

		Equiv. in hydrogen.
Radical constituents	As''' arsenosum -	- H_3
	$(C H_3)'_2$, methyle	- H_2
	Difference -	- H

2. The conjugate radical arsenethyl, $As (C_2 H_5)'_3$, is equivalent to two atoms of hydrogen.

		Equiv. in hydrogen.
Radical constituents	As''''' arsenicum -	- H_5
	$(C_2 H_5)'_3$, ethyle -	- H_3
	Difference -	- H_2

2nd. *The equivalent in hydrogen of a radical conjugated by substitution is equal to the difference between the sum of the equivalents in hydrogen of the constituent radicals and the replaced or absent hydrogen.*

EXAMPLES.

1. The conjugate radical tetrethyl-ammonium, $N(C_2H_5)_4$, is equivalent to one atom of hydrogen.

		Equiv. in hydrogen
Radical constituents	NH_4, ammonium	H
	$(C_2H_5)_4$, ethyle	H_4
		H_5
	Replaced hydrogen	H_4
	Difference	H

2. The conjugate radical acetyle, $C_2H_3(O)$, is equivalent to one atom of hydrogen.

		Equiv. in hydrogen.
Radical constituents	C_2H_5, ethyle	H
	O, oxygen	H_2
		H_3
	Replaced hydrogen	H_2
	Difference	H

451. *Gerhardt's system of classification.*—We have already learned that Gerhardt classifies bodies by types, or according to their chemical functions. We shall now give a list of the more important mineral and organic bodies under their respective types. The compounds are supposed to be derived from types upon which they are considered to be formed. And in the next four chapters we shall give what may be termed the practical applications of Gerhardt's system.

	WATER TYPE. $\left.\begin{matrix}H\\H\end{matrix}\right\}O.$		HYDROCHLORIC ACID TYPE. $HCl.$
	OXIDES.	SULPHIDES (Selenides, Tellurides).	CHLORIDES (Bromides, Iodides, Fluorides).
Derivatives from positive radicals.	**BASES PROPER.** 1. *Primary* or *hydrated bases, e.g.,* hydrate of potash $\left.\begin{matrix}H\\K\end{matrix}\right\}O.$ hydrate of arsenethylium $\left.\begin{matrix}(C_2H_5)_4As\\H\end{matrix}\right\}O.$ 2. *Secondary* or *anhydrous bases, e.g.,* oxide of potassium $\left.\begin{matrix}K\\K\end{matrix}\right\}O.$	**SULPHIDES OF BASES.** 1. *Primary sulphides*, or *sulphhydrides, e.g.,* sulphhydride of potassium $\left.\begin{matrix}K\\H\end{matrix}\right\}S.$ sulphhydride of aniline $\left.\begin{matrix}H_2(C_6H_5)N\\H\end{matrix}\right\}S.$ 2. *Secondary* or *metallic sulphides, e.g.,* sulphide of potassium $\left.\begin{matrix}K\\K\end{matrix}\right\}S.$	**CHLORIDES OF BASES.** 1. *Primary* or *metallic chlorides, e.g.,* chloride of potassium KCl; chloride of aniline $[H_2(C_6H_5)N, Cl]$. . . . .
	ALCOHOLS, or hydrocarburetted bases. 1. *Primary* or *true alcohols, e.g.,* vinic alcohol $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O.$ wood spirit $\left.\begin{matrix}CH_3\\H\end{matrix}\right\}O.$ glycerine $\left.\begin{matrix}C_3H_5O\\H\\H\\H\end{matrix}\right\}O_2.$ 2. *Secondary alcohols*, or *simple ethers, e.g.,* ordinary ether $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O.$	**ALCOHOLIC SULPHIDES.** 1. *Primary sulphides*, or *mercaptans, e.g.,* sulphhydride of ethyl $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S.$ 2. *Secondary sulphides*, or *sulphuretted ethers, e.g.,* sulphide of ethyl $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}S.$	**ALCOHOLIC CHLORIDES.** 1. *Primary chlorides*, or *hydrochloric ethers, e.g.,* chloride of ethyl C_2H_5Cl . . . .
	ALDEHYDS. 1. *Primary aldehyds, e.g.* acetaldehyd $\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}O.$ essence of bitter almonds [illegible]	**ALDEHYDIC SULPHIDES.** 1. *Primary sulphides, e.g.,* sulphobenzol $\left.\begin{matrix}C_7H_5\\H\end{matrix}\right\}S.$ [illegible]ondary sulphides (wanting).	**ALDEHYDIC CHLORIDES.** 1. *Primary chlorides, e.g.,* chloride of aldehyden (from Dutch liquid) C_2H_3Cl. . . . .

HYDROCHLORIC ACID TYPE. H Cl.	AMMONIA TYPE. $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$	HYDROGEN TYPE. H H.
CYANIDES.	NITRIDES (Phosphides).	METALS (Metalloids).
Cyanides of Bases.	Nitrides of Metals.	Metals of Bases.
1. *Primary* or *metallic cyanides, e.g.,* cyanide of potassium K Cy; ferrocyanide of potassium $\{K_2[Fe(CN)_3]''$.	1. *Primary nitrides, e.g.,* amide of potassium $\left.\begin{matrix}K\\H\\H\end{matrix}\right\}N.$	1. *Primary metals*, or *hydrides of metals, e.g.,* hydride of copper $Cu_2\,H$.
. . . . .	2. *Secondary nitrides* (unknown as yet).	2. *Secondary metals*, or *metals properly so called, e.g.,* potassium K K.
. . . . .	3. *Tertiary nitrides, e.g.,* nitride of potassium $\left.\begin{matrix}K\\K\\K\end{matrix}\right\}N.$	
Alcoholic Cyanides.	Alcoholic Nitrides.	Alcoholic Metals.
1. *Primary cyanides*, or *hydrocyanic ethers*, or *nitrides, e.g.,* acetonitrile $C\,H_3\,Cy$.	1. *Primary nitrides, e.g.,* ethylamine $\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N.$	1. *Primary metals*, or *hydrides of the alcohol radicals, e.g.,* marsh gas $C\,H_3,\,H$. benzole $C_6\,H_5\,H$.
. . . . .	2. *Secondary nitrides, e.g.,* diethylamine $\left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}N.$	2. *Secondary metals*, or *alcohol radicals, e.g.,* ethyl $C_2\,H_5,\,C_2\,H_5$. amyl $C_5\,H_{11},\,C_5\,H_{11}$.
. . . . .	3. *Tertiary nitrides, e.g.,* triethylamine $\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}N.$	
. . . . .	. . . . .	Mixed Metals, *e.g.,* zinc-ethyl.
Aldehydic Cyanides.	Aldehydic Nitrides.	Metals of Aldehyds.
1. *Primary cyanides* (not known as yet.)	1. *Primary nitrides.*	1. *Primary metals*, or *hydrides of aldehyds, e.g.,* olefiant gas $C_2\,H_3\,H$.
. . . . .	2. *Secondary nitrides.*	2. *Secondary metals* (not yet obtained).
. . . . .	3. *Tertiary nitrides* (all these classes are as yet unknown).	

	WATER TYPE. $\left.\begin{matrix}H\\H\end{matrix}\right\}O$.		HYDROCHLORIC ACID TYPE. HCl.
	OXIDES.	SULPHIDES (Selenides, Tellurides).	CHLORIDES. (Bromides, Iodides, Fluorides).
Derivatives from negative radicals.	**Acids.** 1. *Primary* or *hydrated acids, e.g.*, sulphuric $\left.\begin{matrix}(SO_2)''\\H_2\end{matrix}\right\}O_2$, benzoic $\left.\begin{matrix}(C_7H_5O)\\H\end{matrix}\right\}O$, cyanic $\left.\begin{matrix}CN\\H\end{matrix}\right\}O$ acids.	**Sulphides of Acids.** 1. *Primary sulphides, e.g.*, hydrosulphocyanic acid $\left.\begin{matrix}(CN)\\H\end{matrix}\right\}S$.	**Chlorides of Acids.** 1. *Primary chlorides*, or *oxychlorides, e.g.*, benzoic oxychloride, or chloride of benzoyl [$(C_7H_5O)Cl$]. free chlorine Cl, Cl. chloride of cyanogen CN, Cl.
	2. *Secondary* or *anhydrous acids, e.g.* benzoic $\left.\begin{matrix}C_7H_5O\\C_7H_5O\end{matrix}\right\}O$, anhydride.	2. *Secondary sulphides, e.g.*, sulphide of benzoyl $\left.\begin{matrix}C_7H_5O\\C_7H_5O\end{matrix}\right\}S$.	. . . . . .
	. . . . . .	. . . . . .	. . . . . .
Derivatives from both positive and negative radicals.	**Oxysalts**, *e.g.*, nitrates $\left.\begin{matrix}NO_2\\K\end{matrix}\right\}O$. sulphates $\left.\begin{matrix}SO_2''\\K_2\end{matrix}\right\}O_2$. cyanates $\left.\begin{matrix}CN\\K\end{matrix}\right\}O$.	**Sulpho-salts**, *e.g.*, sulphocyanides $\left.\begin{matrix}CN\\K\end{matrix}\right\}S$. sulphantimoniate $\left.\begin{matrix}Sb'''\\K\end{matrix}\right\}S_2$.	. . . . . .
	Compound Ethers, *e.g.*, sulphuric ether $\left.\begin{matrix}(SO_2)''\\(C_2H_5)_2\end{matrix}\right\}O_2$. cyanic ether $\left.\begin{matrix}CN\\C_2H_5\end{matrix}\right\}O$.	**Compound Sulphuretted Ethers**, *e.g.*, thiacetate of ethyl $\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}S$. sulphocyanide of ethyl $\left.\begin{matrix}CN\\C_2H_5\end{matrix}\right\}S$.	. . . . . .
	Compound Aldehyds.	**Compound Sulphuretted Aldehyds.**	

HYDROCHLORIC ACID TYPE. HCl.	AMMONIA TYPE. $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N.$	HYDROGEN TYPE. $H\,H$.
CYANIDES.	NITRIDES (Phosphides).	METALS (Metalloids).
Cyanides of Acids.	**Nitrides of Acids.**	**Metals of Acids.**
1. *Primary cyanides, e.g.,* cyanide of benzoyl $(C_7H_5O, CN$. free cyanogen CN, CN.	1. *Primary nitrides, e.g.,* benzamide $\left.\begin{matrix}C_7H_5O\\H\\H\end{matrix}\right\}N.$ succinamide $\left.\begin{matrix}(C_4H_4O_2)''\\H_2\\H_2\end{matrix}\right\}N_2.$	1. *Primary metals,* or *hydro-acids, e.g.,* hydride of benzoyl C_7H_5O, H. hydrochloric acid Cl, H. hydrocyanic acid CN, H.
. . . . .	2. *Secondary nitrides, e.g.,* diacetamide $\left.\begin{matrix}C_2H_3O\\C_2H_3O\\H\end{matrix}\right\}N.$ succinamide $\left.\begin{matrix}C_4H_4O_2''\\C_4H_4O_2''\\H_2\end{matrix}\right\}N_2.$	2. *Secondary metals,* or *radicals, e.g.,* benzoyl C_7H_5O, C_7H_5O. chlorine Cl, Cl. cyanogen CN, CN.
. . . . .	3. *Tertiary nitrides, e.g.,* free nitrogen $\left.N'''\right\}N.$	
. . . . .	**Salts of Amides,** *e.g.,* hydrargo-benzamide $\left.\begin{matrix}C_7H_5O\\Hg\\H\end{matrix}\right\}N.$	In this division many of those already referred to other classes would find their places; such, for instance, as the cyanides of the alcohols, which contain the electro-negative radical (cyanogen) of cyanic acid, and the electro-positive radical of the alcohol.
. . . . .	**Alkalamides,** a term applied by Gerhardt to the amides which contain both an acid radical and an alcohol radical, *e.g.,* ethyl-acetamide $\left.\begin{matrix}C_2H_3O\\C_2H_5\\H\end{matrix}\right\}N.$	

452. The majority of chemists reduce the number of types to three, by regarding the hydrogen and hydrochloric acid types as one; other chemists add to the hydrochloric acid, water, and ammonia types, a fourth, which represents the tetratomic bodies,—marsh gas, $C H_4$, is selected as the type of this group.

453. In the next four chapters the principal organic compounds are classified under their different types; the hydrogen type has been retained, and a different order has been followed in the introduction of the types, in order to render the subject as simple and systematic as possible to the student. The new atomic weights, $C = 12$, $O = 16$, are employed constantly in these chapters; they are not distinguished therefore, as in the former part of the work, by the dark line through the symbol.

NOTE.—(See page 221.)—Wurtz, in noticing Hunt's claim, remarks, "In the history of the science, Griffin should be noticed as having published similar notions, long before Laurent and Hunt. For all this, neither can Laurent or Griffin, any more than Hunt, pass as the author of the theory of types, and I think this is just. Those who discover the facts which give prominence to an idea, and who, thanks to those facts, introduce the idea into science, and who render it fruitful,—these are the true discoverers. Now, the discoverers of the mixed ethers, of the organic anhydrides, and, I may add, of the compound ammonias, are they who have really brought to light the molecular types which characterise modern chemistry. This is why Williamson and Gerhardt have general credit as the authors of this idea. If they are cited in preference to their predecessors, it is in virtue of facts, and of that sort of supremacy which discoveries, properly so called, exert over pure speculation."

CHAPTER VII.

HYDROGEN TYPE.

454. The substances treated under the simple and complex molecules of hydrogen are subdivided into two groups, the Positive and Negative.

SIMPLE MOLECULE.

H H.

POSITIVE GROUP.

455. This group embraces—(1) The hydrides of metals and metals proper. (2) The hydrides of the alcohol radicals and the alcohol metals, pure and mixed.

(1.) HYDRIDES OF METALS (PRIMARY DERIVATIVES).

METALS PROPER (SECONDARY DERIVATIVES).

456. *Primary derivatives.*—Very few hydrides in mineral chemistry are known. One only at present is known, which is formed on the simple molecule; this one is the subhydride of copper, $_{,}Cu_2H$, in which two atoms of copper replace one of hydrogen. This hydride speedily oxidizes by exposure to the air, protoxide of copper and water being formed.

457. *Secondary derivatives.*—The majority of the metals can replace hydrogen atom for atom; that is to say, they are monatomic. The following cannot replace hydrogen in any other proportion; that is to say, they are, in all their combinations, monatomic:—

Na, Na; K, K; L, L; Ca, Ca; Sn, Sn; Ba, Ba; Mg, Mg; Zn, Zn; Cd, Cd.

458. A few of the metals can replace hydrogen by interchange of two atoms of metal for one atom of hydrogen. This tendency is manifested principally by mercury and copper; also, though to an inconsiderable extent, by silver and lead. These semiatomic metals are likewise monatomic; we have therefore to place mercury and copper, *under the simple molecule,* as semiatomic and monatomic; thus,—

$_{,}Hg$, $_{,}Hg$; $_{,}Cu$, $_{,}Cu$. Hg', Hg'; Cu', Cu'.

459. The following metals have also two rates of exchange for hydrogen. We give them here as monatomic metals,—

Pt′, Pt′; Au′, Au′; Cr′, Cr′; Fe′, Fe′; Mn′, Mn′; U′, U′; Pd′, Pd′.

(2.) ALCOHOLIC HYDRIDES. ALCOHOLIC METALS.

1ST CLASS.

(*General Formula of the Radicals of this class* $C_n H_{2n+1}$.)

460. The most general formula of vinic alcohol is that which represents it on the water type; in this formula one atom of the hydrogen in water is replaced by the hydrocarbon C_2H_5, thus $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$; similar formulæ will, therefore, be the most general for all the members in this group of alcoholic bodies. The composition of the hydrocarbon in each alcohol is peculiar to that one; it exists in no other alcohol; it differs from the one in the alcohol next lowest in the series by an increase of CH_2, and from the one next above it by a decrease of CH_2;* thus the formula for the methylic alcohol is $\left.\begin{matrix}CH_3\\H\end{matrix}\right\}O$; the formula for ethylic alcohol, which is next above it in the series, is $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$; and the formula for the alcohol next above, vinic alcohol, is $\left.\begin{matrix}C_3H_7\\H\end{matrix}\right\}O$; the general formula for this group of *alcohol radicals* is $C_n H_{2n+1}$; $C_n H_n$ signifying equal atoms of carbon and hydrogen.

461. When one atom of hydrogen in the molecule of hydrogen is replaced by an atom of one of these alcohol *radicals*, we get the *hydrides* of these radicals. Example.—Hydride of ethyl H, C_2H_5. When the other atom of hydrogen is replaced by a metal, we get a compound formed on the type of the molecule of hydrogen, H H, in which one atom of hydrogen is replaced by a metal, and the other atom by one of the alcohol radicals. Example.—Zinc-ethyle, Zn, C_2H_5. When the two atoms of hydrogen in the molecule of hydrogen are replaced by two

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* A series of analogous substances, whose composition varies by CH_2, or a multiple of it, is called a series of *homologous* bodies. See Appendix A, page 278.

atoms of one of these alcohol radicals, we get the molecule or molecular atom of these radicals, or, as Gerhardt calls them, the *alcohol metals*. Example.—Ethyle-ethyle, C_2H_5, C_2H_5. When the two atoms of hydrogen in the molecule of hydrogen are replaced by different alcohol radicals, we get *mixed alcohol metals*. Example.—Ethyl-amyl, C^2H_5, C_5H_{11}. The hydrides are called, according to Gerhardt, the *primary derivatives*, and the alcohol metals the *secondary derivatives* of hydrogen.

462. We shall now give a list of all the hydrides of the alcohol radicals and all the alcohol metals of this class which have yet been obtained in an isolated state; we shall afterwards see that there are good reasons for believing that the list will be extended.

463. The student must commit to memory the names and symbols of these alcohol radicals; he will then not only be able to write out the formulæ of the alcohol metals and the hydrides, but he will also be prepared to write out all the other combinations of these radicals. These bodies have at present two sets of names; those describing their position in the series, as trityl, tetryl, have been given them by Gerhardt; the others were given at the time of their discovery.

Alcohol metals.

Methyl-methyl	CH_3, CH_3
Ethyl-ethyl	C_2H_5, C_2H_5
Trityl-trityl (Propyl-propyl)	Not isolated (formula will be C_3H_7, C_3H_7)
Tetryl-tetryl (Butyl-butyl) (Valyle-valyle)	C_4H_9, C_4H_9
Amyl-amyl	C_5H_{11}, C_5H_{11}
Hexyl-hexyl (Caprotyle-caprotyle)	C_6H_{13}, C_6H_{13}.

Hydrides of these alcohol radicals.

Hydride of methyl (marsh gas)	H, CH_3
,, ethyl	H, C_2H_5
,, trityl	H, C_3H_7
,, tetryl	H, C_4H_9
,, amyl	H, C_5H_{11}.

464. *Preparation of the hydrides of the alcohol metals.*—These bodies are produced in the putrefaction and dry distillation of vegetable and animal substances. Marsh gas (light carburetted hydrogen), for example, is formed in the destructive distillation of coal, and is also formed by the putrefaction of vegetable matter under water. These hydrides are formed likewise by the action of zinc on the chlorides or iodides of the corresponding alcohol radicals.

Iodide of amyl. Hydride of amyl. Amylene.

$$2\,(C_5H_{11},\ I) + Zn\,Zn = 2\,Zn\,I + H,\,C_5H_{11} + C_5H_{10}.$$

2nd. By the action of water on the compounds of the metals and alcohol metals.

Zinc-ethyl.

$$Zn,\ C_2H_5 + \left.\begin{matrix}H\\H\end{matrix}\right\}O = H,\ C_2H_5 + \left.\begin{matrix}Zn\\H\end{matrix}\right\}O.$$

3rd. They are also formed, as we shall learn hereafter, by distilling the fatty acids with an excess of alkali.

465. *Properties of these hydrides.*—The hydrides at present known, of which a list has been given, are either gases or liquids at the common temperature. The liquid ones are volatilized without decomposition. Chlorine attacks them, removing some of the atoms of hydrogen in the alcohol radical, an equal number of atoms of chlorine being substituted.

$$H,\,C_2H_5 + Cl\,Cl = H,\,C_2\,(H_4\,Cl) + H\,Cl.$$

466. *Preparation of the alcohol metals.*—These bodies can be formed, as we have seen (pars. 198, 206, 208), by the action of zinc on the iodides of the alcohol radicals, at an elevated temperature, and under strong pressure. They are likewise obtained by the action of sodium on the chlorides of the alcohol radicals; and they can also be obtained by the electrolysis of the acids derived from the alcohols. There is disengaged at the same time hydrogen and carbonic acid, and an alkaline carbonate remains. The electrolysis of acetate of potash, for example, gives,—

Acetate of potash. Methyl-methyl. Carbonate of potash.

$$2\,(C_2H_3KO_2) + H_2O = CH_3,CH_3 + H,H + CO_2 + \left.\begin{matrix}(CO)''\\K_2\end{matrix}\right\}O_2.$$

467. *Properties of the alcohol metals.*—Methyl and ethyl are gaseous at the ordinary temperature; the other alcohol metals which have been obtained in an isolated state are liquid bodies, more or less volatile. They exhibit but little tendency to unite with other bodies. The alcohols and ethers cannot be formed from them directly. They are not attacked by hydrochloric acid. Nitric acid only attacks the higher terms of the series, and only then after long ebullition. They are not attacked by potash. Oxygen and sulphur do not act upon them; chlorine and bromine decompose, but do not unite with them, substitution products being formed. (See pars. from 195 to 211.)

468. We have already noticed the way the mixed alcohol metals are prepared (par. 210), and have also given a list of them (page 122).

469. *Mixed Metals.*—The bodies containing a metal proper and an alcohol radical, as zinc-ethyl, zinc-methyl, all contain two or more atoms of metal, combined with two or more atoms of the alcohol radical in two volumes of vapour. They must, therefore, be classified under the polymolecules of hydrogen; we shall therefore notice and describe these bodies under their proper classes. Hitherto we have given the formulæ of zinc-methyl and zinc-ethyl as $C H_3, Zn$, and $C_2 H_5, Zn$, but the true formulæ of these bodies appears to be $\left.\begin{matrix} C H_3 \\ C H_3 \end{matrix}\right\} Zn_2$ and $\left.\begin{matrix} C_2 H_5 \\ C_2 H_5 \end{matrix}\right\} Zn_2$

SECOND CLASS OF ALCOHOL RADICALS.

(*General formula of the radicals of this class,* $C_n H_{2n-1}$.)

470. The only member of this group which has yet been discovered is allyl, $C_3 H_5, C_3 H_5$.

471. *Preparation and properties of allyl.*—When iodide of allyl ($C_3 H_5 I$) is treated with sodium, it is decomposed, iodide of sodium is formed, and allyl is liberated, in the form of a very volatile liquid, possessing an odour resembling that of radishes. It is immediately attacked by chlorine, bromine, and iodine.

THIRD CLASS OF ALCOHOL RADICALS.

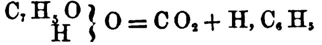
(*General formula of this class of alcohol radicals,* $C_n H_{2n-7}$.)

472. The secondary derivatives or the alcohol metals of this class have not yet been obtained. The following is a list of the primary derivatives or hydrides of this class, which are at present known. They are subdivided into two groups, as the members of the first subdivision do not form aldehydes, whilst the members of the second division do form this class of bodies. The student must commit to memory the names and symbols of these bodies, and their radicals :—

Names.	Formulæ.	Boiling point. F.
First division.		
Benzole* or hydride of phenyle	$H, C_6 H_5$	177°
Xylole	$H, C_8 H_9$	263
Second division.		
Toluole, or hydride of toluene	$H, C_7 H_7$	230
Cumole	$H, C_9 H_{11}$	299
Cymole	$H, C_{10} H_{13}$	341

473. *The hydrides and their preparation.*—The hydrides forming this class are produced in the dry distillation of many organic substances, such as oil, wood, coal, tolu-resin, &c. They are likewise formed by the dry distillation of the monobasic acids $C_n H_{2n-9} O$ with excess of lime or baryta, a carbonate of the base being formed at the same time. Example :—

Hydride of phenyle, or benzole.



$$\left.\begin{array}{c} C_7 H_5 O \\ H \end{array}\right\} O = C O_2 + H, C_6 H_5$$

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* As benzole has become a substance of great commercial value, it is important to be able readily to detect it in a mixture of other hydrocarbons. The following is Dr. Hofmann's method :—"A drop of benzole is heated in a small test-tube, with fuming nitric acid, to convert it into nitro-benzole. A good deal of water is then added, to precipitate the nitro-benzole in small drops, which must be taken up by ether. The etherial solution is then poured into another small test-tube, and equal volumes of alcohol and dilute hydrochloric acid are added; a few fragments of granulated zinc are then dropped in. In about five minutes, sufficient hydrogen will have been disengaged to produce aniline, which will be found combined with the acid. The liquid is supersaturated with an alkali, and shaken with ether, which dissolves the aniline set free. A drop of this etherial solution allowed to evaporate on a watch-glass, and mixed, after the evaporation of the ether, with a drop of a solution of hypochlorite of lime, will show the *violet tints* which are characteristic of aniline. The operation may be executed very rapidly, and without difficulty."

474. Toluole and cymole are also formed by the distillation of their respective alcohols with an alcoholic solution of potash. Cymole is contained ready formed in the essence of cummin.

475. *Properties of these hydrides.*—This class of hydrides, at the ordinary temperature, are liquids. They are volatile without decomposition, and they are solidified by the cold.

(1.) Treated with sulphuric anhydride, they give sulpho-conjugated hydrides:—

Two atoms of hydride of phenyle.

$$2\,(H, C_6 H_5) + O, S O_2, = H_2\,(C_6 H_4)_2\ S O_2 + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

(2.) Treated with concentrated sulphuric acid, they are transformed into sulpho-conjugated monobasic acids:—

$$H, C_6 H_5 + \left.\begin{matrix}(S O_2)''\\H_2\end{matrix}\right\}O_2 = \left.\begin{matrix}C_6 H_5 (S O_2)\\H\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

(3.) Treated with fuming nitric acid, or with a mixture of concentrated nitric and sulphuric acids, they produce nitro-conjugated or binitro-conjugated hydrides:—

Nitro-benzole.

$$(1)\quad H, C_6 H_5 + \left.\begin{matrix}N O_2\\H\end{matrix}\right\}O = H, C_6 H_4 (N O_2) + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

$$(2)\quad H, C_6 H_5 + 2\left(\left.\begin{matrix}N O_2\\H\end{matrix}\right\}O\right) = H, C_6 H_3 (N O_2)_2 + 2\left.\begin{matrix}H\\H\end{matrix}\right\}O$$

These nitro-conjugated products, as we shall see hereafter, are transformed by reducing agents into organic alkalies.*

(4.) When these hydrides are submitted to the action of chlorine and bromine, they fix directly these elements, producing chloro-conjugated chlorhydrates.

$$H, C_6 H_5 + Cl_3 Cl_3 = \left.\begin{matrix}C_6 H_2 (Cl_3)\\H_3\end{matrix}\right\}\begin{matrix}H\\Cl_3\end{matrix}$$

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* By the reduction of nitro-benzole, aniline is formed, from which organic alkali all the beautiful new colours—mauve, roseine, &c.—are formed. The nitro-benzole is therefore manufactured on a large scale, and it is accomplished in the following way:—"A fine stream of benzole and another of the strongest nitric acid are allowed to run together in a worm, or long glass tube, kept well cooled. The two liquids react on each other on coming in contact, heat is disengaged, and nitro-benzole is formed. Commercial nitric acid, mixed with half its volume of sulphuric acid, may be substituted for the concentrated nitric acid. The nitro-benzole collected at the end of the worm is first washed with water, then with a solution of carbonate of soda, and afterwards once again with water."—Kopp, "On the Preparation of Artificial Colouring Matters." *Chemical News*, vol. ii.

An alcoholic solution of potash halves these chloro-conjugated chlorhydrates into chloro-conjugated hydrates and hydrochloric acid.

$$\left.\begin{matrix}C_6\,H_2\,(Cl_3)\\H_3\end{matrix}\right\}\begin{matrix}H\\Cl_3\end{matrix} = H,\ C_6\,H_2\,(Cl_3) + 3\ H\,Cl$$

NEGATIVE GROUP.

476. This group embraces—(1) The monatomic acid radicals, simple and compound. (2) The aldehydes. (3) The ketones.

(1.) ACID RADICALS, SIMPLE AND COMPOUND.

477. The hydrides of these acid radicals, which might be termed the primary derivatives, come under the type of hydrochloric acid; we therefore only here give the formulæ of the simple molecules of these bodies.

Chlorine.	Bromine.	Iodine.	Cyanogen.
Cl, Cl	Br, Br	I, I	Cy, Cy

(2.) ALDEHYDES, OR THE HYDRIDES OF THE ACID RADICALS.

478. Common or acetic aldehyde, C_2H_4O, is obtained by the oxidation or dehydrogenation of alcohol, C_2H_6O, whence its name aldehyde, from *alcohol dehydrogenatus*. The term is now applied to a class of bodies which have the same relation to their respective *oxacids* that common aldehyde has to acetic acid. The constitution of these bodies is still a matter of doubt; Liebig regards the organic aldehydes as the hydrated oxides of electro-negative radicals, just as alcohols are, according to his view, the hydrated oxides of electro-positive radicals. This radical theory assumes, therefore, that there exists in common aldehyde a radical called *acetyle*, or *aldehydene*, $= C_4H_3$, which, in combination with one atom of oxygen, forms the *oxide of acetyle;* and the latter, in combination with one atom of water, forms *aldehyde*, or *hydrated oxide of acetyle*$=$HO, C_4H_3, O; in these formulæ the old equivalent numbers of C and O are employed, $C = 6$ and $O = 8$.

479. The aldehydes are represented in two different ways according to the new view. Some chemists represent them on the type water; the formula of common aldehyde is then, according to this view, $\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}O$: other chemists repre-

sent them on the type of hydrogen; the formula of common aldehyde is, according to this view, C_2H_3O, H; the acid-oxygenized radical, C_2H_3O, occupying the place of one atom of hydrogen in a molecule of that element. As we shall view them as constructed on the hydrogen type, we will here show in what a satisfactory manner their production and oxidation can be explained according to the hydrogen type construction.

Production.

$$\left.\begin{array}{ll}\text{Alcohol (water type) -} & = \left.\begin{array}{c}C_2H_5\\ H\end{array}\right\}O\\ \text{Oxygen - - - - -} & \quad O\end{array}\right\} = \left\{\begin{array}{l}C_2H_3O, H = \left\{\begin{array}{l}\text{aldehyde*}\\ \text{(hydrogen type)}\end{array}\right.\\ \left.\begin{array}{c}H\\ H\end{array}\right\}O.\end{array}\right.$$

Oxidation.

$$\left.\begin{array}{ll}\text{Aldehyde (hydrogen type)} & = C_2H_3O, H\\ \text{Oxygen - - -} & \quad\quad O\end{array}\right\} = \left\{\begin{array}{c}C_2H_3O\\ H\end{array}\right\}O = \left\{\begin{array}{l}\text{acetic acid}\\ \text{(water type).}\end{array}\right.$$

480. Alcohol, by oxidation, separates into water and a body (aldehyde) on the hydrogen type; as hydrogen yields, by oxidation, water, so aldehydic bodies yield, by oxidation, bodies (acids) constructed on the water type; and as hydrogen is produced by the deoxidation of water, so aldehydes are produced by the deoxidation of those acid bodies which have been produced by their oxidation.

481. The aldehydes are *monatomic*, *biatomic*, or *triatomic*, that is to say, they are derived from one, two, or three molecules of hydrogen, according as their corresponding acids are derived from one, two, or three molecules of water.

482. The following compounds may be regarded as the aldehydes of some of the monobasic mineral acids:—

Nitrous acid, or aldehyde of nitric acid	$HO_2N = H, NO_2$
Hydrochloric acid, or aldehyde of hypochlorous acid - - - -	$HCl = H, Cl$
Hydrocyanic acid, or aldehyde of cyanic acid - - - - -	$HCN = H, Cy$
Spontaneously inflammable phosphide of hydrogen, or aldehyde of hypophosphorous acid - - - -	$HP = H, P$

---

[*] Since this was written, Wurtz has converted aldehyde into alcohol by the direct addition of hydrogen; this experiment supports the view that the aldehydes are formed on the water type. Wurtz converted aldehyde into alcohol by submitting an aqueous solution of aldehyde to the action of sodium amalgam.—See *Repert. de Chimie*, vol. iv. p. 226.

ALDEHYDES CORRESPONDING TO THE FIRST CLASS OF ALCOHOL RADICALS.

(*General formula of the acid radical in this class of aldehydes,* $C_nH_{2n-1}O$.)

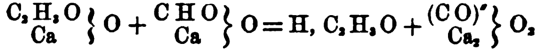
483. We shall only give the composition of two aldehydes in this class; the student will be required to write out the formulæ of the others.

Acetic aldehyde (aldehyde *par excellence*)	H, C_2H_3O
Butyric aldehyde - - - - -	H, C_4H_7O

484. *Preparation.*—When the alcohols are burned with free access of air, the sole products are water and carbonic acid; but when the supply of air is limited, and the oxidation is effected at a lower temperature, the principal product is an aldehyde. The most convenient method of oxidizing the alcohol, so as to produce an aldehyde, is by submitting to distillation a mixture of alcohol, sulphuric acid, and binoxide of manganese or bichromate of potash.

485. The following is a still more general method for preparing these bodies; it consists in the dry distillation of an intimate mixture of equal equivalents of formiate of lime and the lime salt of the organic acid, the aldehyde of which we wish to obtain. Thus, to obtain acetic aldehyde we distil, in the dry state, equal equivalents of formiate and acetate of lime.

Acetate of lime. Formiate of lime. Carbonate of lime.



$$\left.\begin{matrix}C_2H_3O\\Ca\end{matrix}\right\}O+\left.\begin{matrix}C\,H\,O\\Ca\end{matrix}\right\}O=H,C_2H_3O+\left.\begin{matrix}(C\,O)''\\Ca_2\end{matrix}\right\}O_2$$

486. Enanthylic aldehyde is obtained by the distillation of castor oil; and caprylic aldehyde is obtained by the distillation of that oil with potash.

487. *Physical properties of these bodies.*—They are liquid or solid bodies. Many of them (acetic, enanthylic, &c.) form two or three isomers.

488. *Chemical properties.*—The aldehydes combine directly with oxygen, and become transformed by this oxidation into monobasic acids; the general formula of the acids formed by the oxidation of this class of aldehydes is $\left.\begin{matrix}C_nH_{2n-1}O\\H\end{matrix}\right\}O$. On account of their great affinity for oxygen, they reduce readily oxide of silver. When

we heat slightly a solution of nitrate of silver, to which a few drops of ammonia must be added, so as to render it slightly alkaline, in a glass tube, or other glass vessel, and add a little aldehyde, immediately there is deposited on the inner sides of the vessel a most beautiful metallic mirror. The aldehyde robs the oxide of silver of its oxygen, and becomes itself transformed by the appropriation of that element into its corresponding acid. The silver is thus liberated in a very finely divided state, and is deposited on the glass in a smooth, united, compact layer. It was supposed, at one time, that acetic aldehyde was converted, in this reaction, into a particular acid, named acetous or aldehydic, but this is not the case; it is converted into acetic acid. When an aldehyde is treated with one of the fixed alkalies, and the solution warmed, it yields its corresponding acid, and also a resinous matter, which has not been examined. They enter into direct union with ammonia. The compounds thus produced are frequently crystallizable. This property is made use of in separating the aldehydes from other bodies. We give the formation and the composition of aldehyde of ammonia as the type of the series:—

$$H, C_2 H_3 O + N H_3 = C_2 H_4 O, N H_3$$

Another characteristic property of the aldehydes is that of uniting with the alkaline bisulphites, especially those of soda and ammonia, and forming with them crystallizable compounds. This property of combining with alkaline bisulphites is not limited to this class; it is possessed by all the aldehydes. This property is made use of in separating aldehydes from complex mixtures. We give the formula of the compound produced by the combination of bisulphite of ammonia and acetic aldehyde, as an example of the composition of this class of bodies, $C_2 H_4 O, N H_3 S O_2$. The chemical properties we have now described are very characteristic of the aldehydes.

489. When the compounds produced by the combination of ammonia with the aldehydes are acted upon by sulphide or selenide of hydrogen, they are converted into sulphuretted bases:—

$$3\,(C_2H_4O, NH_3) + 3H_2S = \overset{\text{Thialdine.}}{C_6H_{13}NS_2} + 3H_2O + (NH_4)_2S$$

490. When they are treated with hydrocyanic and hydrochloric acids, they also give rise to organic bases:—

Alanine.
(Propionamic acid.)

$$C_2H_4O + HCN + H_2O = C_3H_7NO_2$$

and these organic bases are transformed by nitrous acid into biatomic acids,—

Lactic acid.

$$2\,C_3H_7NO_2 = 2\,C_3H_6O_3 + 2\,N_2 + H_2O$$

491. The aldehydes disengage hydrogen in contact with potassium, the latter body occupying its place:—

$$2\,(H, C_2H_3O) + KK = 2\,(K, C_2H_3O) + HH$$

492. The hydrogen can also be replaced by chlorine. We then get the chloraldehydes, which will be noticed under the head of hydrochloric acid, as they come under that type. The oxygen can also be replaced by sulphur. We then get sulphaldehydes; and, lastly, the hydrogen in the acid radical can be replaced by chlorine, bromine, &c.

ALDEHYDES CORRESPONDING TO THE SECOND CLASS OF ALCOHOL RADICALS.

(*General formula of the acid radicals in this class of aldehydes,* $C_nH_{2n-3}O$.)

493. As yet we only know one aldehyde (acrolein) belonging to this series,—

Acrylic aldehyde (acrolein) - - H, C_3H_3O

494. *Preparation.*—When glycerin, or any oil or fat containing it, is distilled, vapours are formed which violently attack the eyes and the organs of respiration. This body has therefore been appropriately called acrolein. It is best prepared by distilling, in a capacious retort, glycerin with phosphoric anhydride, or with bisulphate of potash. These bodies dehydrate or remove the elements of water from the glycerin. By this removal it becomes converted into acrolein, as glycerin contains the elements of this latter body, and two equivalents of water:—

Glycerin.

$$C_3H_8O_3 = C_3H_4O + 2\,H_2O.$$

It is also formed by the oxidation of its corresponding alcohol.

495. *Properties.*—It is a thin, colourless, highly volatile liquid, lighter than water, and boiling at 126° F. Its vapour is irritating beyond description. It is sparingly soluble in water, freely in alcohol and ether. It unites directly with oxygen; with ammonia, it reduces oxide of silver, and forms a resinous body with potash, like the previous aldehydes.

ALDEHYDES CORRESPONDING TO THE THIRD CLASS OF ALCOHOL RADICALS.

(*General formula of the acid radicals in this class of aldehydes,* $C_n H_{2n-9} O$.)

496. We have already noticed that the first division of the third series of alcohol radicals do not form aldehydes. This character distinguishes them from the members of the second division, which do form this class of bodies. The following is a list of those at present known:—

Hydride of benzoyl (essence of bitter almonds) - - - - -	$H, C_7 H_5 O$
Hydride of toluyl - - - -	$H, C_8 H_7 O$
Hydride of cumyl (essence of cumin)	$H, C_{10} H_{11} O$

497. *Preparation.*—This class of aldehydes is produced by the oxidation of their corresponding alcohols. Hydride of cumyl exists naturally in plants; oil of almonds is obtained by the fermentation of amygdaline, hydrocyanic acid and grape sugar being also formed. They can also be obtained by distilling a mixture of formiate of lime and the lime salt of the corresponding acid together (par. 485).

498. *Properties.*—They behave with oxygen like the other aldehydes. They are transformed by potash into the corresponding monobasic acids. This class of aldehydes, and also the aldehydes of the fourth and fifth classes, combine with ammonia, forming neutral compounds, which are named in the following way,—hydrobenzamide, hydrocinnamide, &c. These neutral compounds, when boiled with a somewhat dilute solution of caustic potash, or when simply exposed to a temperature of 140°—160° C., become transformed, without any evolution of ammonia, into organic bases, *having the same composition*

as the original amide compounds. These amides, when treated with sulphide of hydrogen, yield the aldehyde, but with sulphur substituted for the oxygen.

499. When benzoic aldehyde is evaporated with hydrocyanic and hydrochloric acids, we obtain formobenzoic acid:—

Formobenzoic acid.

$$2\,C_7H_6O + 2\,HCN + 4\,H_2O = 2\,NH_3 + C_{16}H_{16}O_6$$

500. An atom of hydrogen in the radical of these aldehydes can be replaced by NO_2. Example:—Aldehyde of nitrobenzoyl, $H, C_7H_4(NO_2)O$. These compounds are transformed by potash into the corresponding nitro-acids; and by ammonia into nitro-amide compounds.

FOURTH CLASS OF ALDEHYDES.

(*General formula of the acid radicals in this class of aldehydes,* $C_nH_{2n-11}O$.)

501. *The hydrides of the alcohol radicals and the alcohol metals* corresponding to this class of aldehydes have not been isolated, and only one aldehyde belonging to the class has been discovered; it bears, as the student will see, the same relation to the preceding class as the allyl class does to the vinic one.

Hydride of cinnamyl (oil of cinnamon), H, C_9H_7O.

502. Essence of cinnamon and essence of cassia consist chiefly of this aldehyde.

503. *Properties.*—It behaves with oxygen, potash, and the bisulphites like the previous aldehydes. It is often converted, in its decompositions, into hydride of benzoyl, and the hydride of benzoyl can also be converted into it; for instance, if hydride of cinnamyl be boiled with nitric acid, hydride of benzoyl is evolved, and benzoic acid is found in the solution; and if hydride of benzoyl be dissolved in aldehyde, and the solution saturated with hydrochloric acid gas, and afterwards distilled, oil of cinnamon is found in the distillate; hydride of cinnamyl may, in fact, be regarded as hydride of benzoyl, in which an equivalent of hydrogen has been replaced by an equivalent of acetyl. Example:—$H, C_7H_4(C_2H_3)O$.

FIFTH CLASS OF ALDEHYDES.

(*General formula of the acid radicals in this class of aldehydes,* $C_n H_{2n-9} O_2$.)

504. The hydrides of the alcohol radicals and the alcohol metals of this class have not been isolated. The aldehydes of this class differ only from those in the third class in the quantity of oxygen they contain; the relative proportion of the carbon and hydrogen is the same, and they increase also, like the third class, in the proportion of $C H_2$.

Hydride of salicyl (salicylous acid), $H, C_7 H_5 O_2$
Hydride of anisyl - - - - $H, C_8 H_7 O_2$.

505. *Preparation.*—Salicylous acid is found as the chief ingredient in the essence of meadowsweet; it is separated from the hydrocarbon which accompanies it by treating the crude essence with solution of potash; the acid combines with the potash, whilst the hydrocarbon is distilled; the potash compound, on being distilled with a slight excess of dilute sulphuric acid, yields the hydride pure. It is also obtained by distilling one part of salicine, one part of bichromate of potash, two and a half of oil of vitriol, and twenty of water, together. When oil of aniseed is acted upon by dilute nitric acid, a reddish oil is obtained, consisting of a mixture of anisic acid and hydride of anisyl; if the oil, after being washed with a weak solution of potash in order to remove the anisic acid, be cautiously distilled, the hydride passes over pure.

506. *Properties.*—The hydride of salicyl possesses the characters of an acid; it decomposes the carbonates with effervescence, yielding crystallizable salts; one or more atoms of hydrogen in the radical of salicylous acid can be replaced by chlorine, bromine, or $N O_2$; the bodies produced by these substitutions likewise possess acid properties, and are capable of forming salts. One or more atoms of hydrogen in the radical, anisyl, can also be replaced by Cl, Br, or $N O_2$; but this hydride has not been so much studied as salicylous acid. Both aldehydes combine with ammonia and with the bisulphites.

(3.) KETONES (ACETONES).

507. The constitution of these bodies is still, like the constitution of the aldehydes, a matter of doubt. Some

chemists represent them on the type water; others represent them on the hydrogen type. We will formulate acetone, the best known member of the family of the ketones, on both these types, so as to make the student acquainted with the prevailing views on the constitution of this class of bodies. On the type of water the formula of acetone is $\left.\begin{matrix}C_2H_3\\CH_3\end{matrix}\right\}O$. According to this formula the ketones are bodies in which the atoms of hydrogen in water have been all replaced by *different* hydrocarbon radicals. On the type of hydrogen the formula of acetone is $\begin{matrix}C_2H_3O.\\CH_3\end{matrix}$ According to this formula, the ketones are conjugated aldehydes, in which the equivalent of hydrogen is replaced by one of the alcohol radicals.

508. *Preparation of the ketones.*—The ketones are prepared by submitting to destructive distillation a metallic salt, in the anhydrous state, of the corresponding acid of the series. The acid is decomposed into the ketone and carbonic acid; this latter body remains combined with the metal, if it be one of the alkaline metals, or a metal of the alkaline earths; if not, it is evolved along with the ketone. We will give the decomposition which occurs when acetate of lime is submitted to destructive distillation, as the representative of the decompositions which the salts of the other acids of the series undergo.

$$2\left(\left.\begin{matrix}C_2H_3O\\Ca\end{matrix}\right\}O\right)=\left.\begin{matrix}C_2H_3O\\CH_3\end{matrix}\right\}+\left.\begin{matrix}(CO)''\\Ca_2\end{matrix}\right\}O_2$$

509. As the ketones have only been very incompletely studied, we shall not describe their properties, but simply give the formulæ of a few of them.

Ketones corresponding to the first class of alcohol radicals, and to the first class of aldehydes.

*Acetone (aceta-acetone) - -	CH_3, C_2H_3O
Propione - - - - -	C_2H_5, C_3H_5O

---

* Fridel has converted acetone, by the direct addition of hydrogen, into propylic alcohol, or an alcohol isomeric with it; he effected this conversion in the same way as Wurtz effected the conversion of aldehyde into alcohol, viz., by treating an aqueous solution of acetone with sodium amalgam.—See *Repert. de Chimie*, vol. iv. p. 351.

510. Ketones corresponding to the alcohol radicals of the third classs, and to the aldehydes of the third class.

Benzophenone - - - - C_6H_5, C_7H_5O

511. The acetones combine, like the aldehydes, with the alkaline bisulphites.

512. The acetones appear to combine with ammonia, like the aldehydes, forming, like them, with the ammonia, basic compounds. As yet only acetone has been submitted to this process.

$$2\,H_3N = 3\,C_3H_6O = (C_9H_{18})'''' \big\} N_2 + 3\,H_2O.^*$$

EXERCISE.

133. Write out the formulæ for the following substances:—Propionic aldehyde, valeraldehyde, capric aldehyde, enanthylic aldehyde, butyracetone (butyrone), valeracetone, pelargonic aldehyde, enanthylone.

DOUBLE MOLECULE.

$H_2, H_2.$

POSITIVE GROUP.

513. This group embraces—(1) The biatomic metals. (2) The radicals of the biatomic alcohols. (3) Compounds of metals with monatomic alcohol radicals.

(1.) HYDRIDES OF METALS (PRIMARY DERIVATIVES). METALS PROPER (SECONDARY DERIVATIVES).

514. *Primary derivatives.*—No hydride of any of the metals is known which is formed on the double molecule.†

515. *Secondary derivatives.*—Palladium, platinum, titanium, and tin are the principal biatomic metals; the first two we have noticed act sometimes as monatomic metals, and the last two sometimes act as tetratomic metals.

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* The student must omit the Exercise, and the rest of this chapter, and pass on to Chapter VIII., commencing at par. 541.

† Quite recently Wanklyn and Carius have obtained hydride of iron, which has the following composition, Fe_2H_2. They obtained it by acting upon zinc-ethyl with iodide of iron; thus,—

$$Zn_2(C_2H_5)_2 + Fe_2I_2 = 2\,ZnI + Fe_2H_2 + 2\,(C_2H_4).$$

(2.) Radicals of the Biatomic Alcohols.

(*General formula*, $C_n H_{2n}$.)

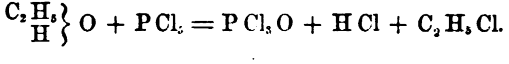
516. Very different views are taken of the rational constitution of this class of hydrocarbons. Liebig regards them as the hydrides of the radicals, $C_n H_{2n-1}$. They might also be regarded as the hydrides of the alcohol radicals of the second class; for instance, propylene, $C_3 H_6$, might be regarded as the hydride of allyl, H, $C_3 H_5$. But it will be seen, as we proceed, that there is good reason for viewing them as positive radicals, capable of replacing, and possessing the functions of, two atoms of hydrogen; viewed in this light they are diatomic radicals.

517. When these bodies are submitted to the action of chlorine, several chlorine derivatives can be obtained; but in order to show the student how the constitution of these bodies was unravelled, we will here direct his attention to only one of these chlorine compounds at present, and we will take one member (ethylene, $C_2 H_4$) of the group, as less confusing to the student than if we were to allude to the entire group. When equal volumes of ethylene and chlorine are added together, they combine, and give rise to a compound called Dutch liquid, which may be formulated thus, $C_2 H_4 Cl_2$; there has, therefore, been a direct combination between the chlorine and the hydrocarbon, unattended with any substitution; if this compound be treated with an alcoholic solution of potash, it parts with the elements of hydrochloric acid; it was therefore inferred that the rational formula of this chlorine compound was not $C_2 H_4 Cl_2$, but $C_2 H_3 Cl$, $H Cl$. This was the view chemists took of the constitution of Dutch liquid, until M. Wurtz proved, by the most elegant and convincing experiments, that its correct formula is $C_2 H_4 Cl_2$.

Constitution of Dutch liquid, according to M. Wurtz.

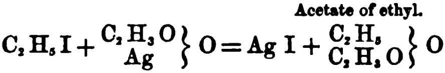
518.—1st. If we treat ordinary vinic alcohol with pentachloride of phosphorus, we obtain chloride of ethyl, thus:—

Chloride of ethyl.



$$\left.\begin{matrix}C_2 H_5 \\ H\end{matrix}\right\} O + P Cl_5 = P Cl_3 O + H Cl + C_2 H_5 Cl.$$

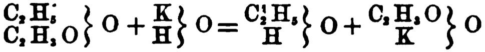
2nd. If we act upon this chloride ethyl, or, more conveniently, upon the bromide or iodide of ethyl, with acetate of silver, we obtain acetate of ethyl, thus:—



Acetate of ethyl.

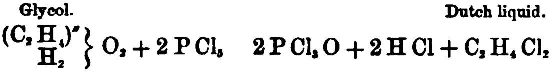
$$C_2H_5I + \left.\begin{matrix}C_2H_3O\\ Ag\end{matrix}\right\} O = Ag\,I + \left.\begin{matrix}C_2H_5\\ C_2H_3O\end{matrix}\right\} O$$

3rd. If we treat acetate of ethyl with potash, we reproduce alcohol, thus:—



$$\left.\begin{matrix}C_2H_5\\ C_2H_3O\end{matrix}\right\} O + \left.\begin{matrix}K\\ H\end{matrix}\right\} O = \left.\begin{matrix}C_2H_5\\ H\end{matrix}\right\} O + \left.\begin{matrix}C_2H_3O\\ K\end{matrix}\right\} O$$

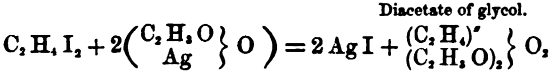
519.—1st. Parallel reactions are produced if, in place of the vinic alcohol, which is monatomic, we operate upon glycol, which is a biatomic alcohol. Thus, if we act upon glycol with pentachloride of phosphorus, we obtain Dutch liquid:—



Glycol. Dutch liquid.

$$\left.\begin{matrix}(C_2H_4)''\\ H_2\end{matrix}\right\} O_2 + 2\,PCl_5 \quad 2\,PCl_3O + 2\,HCl + C_2H_4Cl_2$$

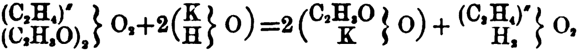
2nd. If we treat Dutch liquid, or the corresponding iodine or bromine compound, with acetate of silver, we obtain acetic glycol ether (diacetate of glycol), thus:—



Diacetate of glycol.

$$C_2H_4I_2 + 2\left(\left.\begin{matrix}C_2H_3O\\ Ag\end{matrix}\right\} O\right) = 2\,AgI + \left.\begin{matrix}(C_2H_4)''\\ (C_2H_3O)_2\end{matrix}\right\} O_2$$

3rd. If we treat diacetate of glycol with potash, we regenerate the biatomic alcohol glycol, thus:—



$$\left.\begin{matrix}(C_2H_4)''\\ (C_2H_3O)_2\end{matrix}\right\} O_2 + 2\left(\left.\begin{matrix}K\\ H\end{matrix}\right\} O\right) = 2\left(\left.\begin{matrix}C_2H_3O\\ K\end{matrix}\right\} O\right) + \left.\begin{matrix}(C_2H_4)''\\ H_2\end{matrix}\right\} O_2$$

520. From comparison of these facts, it is proved that Dutch liquid is to glycol that which chloride of ethyl is to vinic alcohol; and that, by consequence, Dutch liquid is the ether chloride of glycol, or chloride of ethylene, which is the chemical name by which it is now known.

521. The following is a list of the radicals, C_2H_{2n}, which have been produced from the vinic alcohol series:—

Names.	Formulæ.		Boiling point, F.
Methylene	$C\ H_2$	Gas	
Olefiant gas (ethylene)	$C_2\ H_4$	„	
Tritylene (propylene)	$C_3\ H_6$	„	
Oilgas (tetrylene, butylene)	$C_4\ H_8$	„	
Amylene	$C_5\ H_{10}$	Liquid	102°
Hexylene (caproylene)	$C_6\ H_{12}$	„	131
Heptylene (œnanthylene)	$C_7\ H_{14}$	„	122
Octylene (caprylene)	$C_8\ H_{16}$	„	257
Nonylene (elaene)	$C_9\ H_{18}$	„	230
Paramylene	$C_{10}\ H_{20}$	„	320
Cetylene	$C_{16}\ H_{32}$	„	527

522. *Preparation of these hydrocarbons.*—These bodies are produced by the action of an excess of concentrated sulphuric acid, or chloride of zinc, or other bodies which have a strong affinity for water, on the corresponding alcohols (alcohols of the vinic series) at a high temperature; the alcohols become converted, by the abstraction of the elements of water, into these hydrocarbons, thus :—

Vinic alcohol. Ethylene.

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O-\left.\begin{matrix}H\\H\end{matrix}\right\}O=C_2H_4$$

523. These hydrocarbons are also formed along with the alcohol radicals when the iodides of the alcohol radicals are acted upon by zinc (195). These hydrocarbons are also formed in the destructive distillation of organic substances; several of them being found among the products of the distillation of coal.

524. In some cases the hydrocarbon, $C_n\,H_{2n}$, which is obtained, appears to be coupled, for it has a vapour-density double of that which it ought to possess. For example, the vapour of the hydrocarbon obtained in distilling amylic alcohol, $\left.\begin{matrix}C_5H_{11}\\H\end{matrix}\right\}O$, with $\left.\begin{matrix}(SO_2)''\\H_2\end{matrix}\right\}O_2$, has a density exactly double of that obtained by distilling the same alcohol with chloride of zinc; therefore, if the equivalent of the latter be represented by $C_5\,H_{10}$, the equivalent of the hydrocarbon obtained by the action of sulphuric acid must be $C_{10}\,H_{20}$: the hydrocarbon in this case has therefore suffered condensation, and has been converted into the polymeric paramylene.

525. *Properties.*—These bodies combine readily with sulphuric anhydride, and with pentachloride of antimony. They are also absorbed by oil of vitriol, and the solution, when diluted with water and distilled, yields the corresponding monatomic alcohol in the vinic series. They also combine, as we have already noticed, with two equivalents of chlorine, bromine, or iodine, forming compounds, the best known of which is Dutch liquid. They are especially distinguished by this property of combining with two equivalents of these metalloids. The property of being dissolved by sulphuric acid, and of forming liquid compounds with chlorine and bromine, is made available for separating olefiant gas, and the other more volatile hydrocarbons of the series, from other gaseous bodies (see exercise 92, page 73). If, after these chlorine compounds, $C_n H_{2n} + Cl_2$, have been obtained, we continue to act upon the body with chlorine, we can finally remove all the hydrogen, replacing it by chlorine. Olefiant gas is distinguished from the other gaseous members of the group by solidifying into a solid crystalline mass on being exposed to a freezing mixture.

526. The hydrides of the alcohol radicals, $C_n H_{2n+1}$, and also the hydrides of the other alcohol radicals, are capable of furnishing, by the fixation of one equivalent of oxygen, a corresponding series of monatomic alcohols. These hydrocarbons, which we have represented by the formula $C_n H_{2n}$, also furnish, by the fixation of one atom of oxygen, a corresponding series of monatomic alcohols. But these hydrocarbons of the formula $C_n H_{2n}$ furnish, by the fixation of one atom of water, another series of monatomic alcohols. This fixation of water has not yet been accomplished with the marsh gas series. Olefiant gas and its homologues furnish these two series of monatomic alcohols, whilst marsh gas and its homologues have only yet furnished one series, thus:—

MARSH GAS SERIES. OLEFIANT GAS SERIES.

By the fixation of one equivalent of oxygen.

Hydride of methyl.	Methylic alcohol.	Propylene.	Allylic alcohol.

$$H, CH_3 + O = \left.\begin{matrix} CH_3 \\ H \end{matrix}\right\} O \quad \Big| \quad C_3H_6 + O = \left.\begin{matrix} C_3H_5 \\ H \end{matrix}\right\} O$$

MARSH GAS SERIES. OLEFIANT GAS SERIES.

By the fixation of one equivalent of oxygen.

Hydride of ethyl. Vinic alcohol.

$$H, C_2 H_5 + O = \left.\begin{matrix} C_2 H_5 \\ H \end{matrix}\right\} O$$

Hydrides of the radicals, $C_n H_{2n-7}$

Toluole. Benzoyl-alcohol.

$$H, C_7 H_7 + O = \left.\begin{matrix} C_7 H_7 \\ H \end{matrix}\right\} O$$

By the fixation of one atom of water.

Olefiant gas. Vinic alcohol.

$$C_2 H_4 + H_2 O = \left.\begin{matrix} C_2 H_5 \\ H \end{matrix}\right\} O$$

Propylic alcohol.

$$C_3 H_6 + H_2 O = \left.\begin{matrix} C_3 H_7 \\ H \end{matrix}\right\} O$$

527. The fixation of the one equivalent of oxygen cannot yet be effected directly, but is accomplished by a series of substitution processes. The fixation of water by olefiant gas and its homologues is accomplished by absorbing them by sulphuric acid, adding water and then distilling.

528. These hydrocarbons, $C_n H_{2n}$, are striking examples that the same body can have more than one rational formula; we have already noticed that they can be looked upon as the hydrides of the aldehyde radicals, if we represent the aldehydes on the water type. As they behave in every respect like the marsh gas series with oxygen, giving rise to alcohols of the allylic series, they may be looked upon as the hydrides of the alcohol radicals of this series of alcohols. By their conversion into the vinic series of alcohols by the fixation of water they play the part of monatomic hydrocarbons of the general formula $C_n H_{2n}$. And, lastly, they play the part of diatomic radicals in the diatomic alcohols.*

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* The chemical atom of these bodies occupies two volumes, and it is also evident, from many of their chemical reactions, as, for instance, their uniting directly with chlorine, &c., that their atoms in the free state are not united in pairs. See foot-note, p. 232.

(3.) Compounds of Metals with Monatomic Radicals.

529. We have already very frequently pressed on the attention of the student that the formulæ of bodies, according to the new views, are regulated by their vapour-densities; it is assumed that the molecules of all bodies occupy two volumes in the gaseous state. Now, all the volatile compounds of metals with the monatomic radicals, contain an *even* number of equivalents of metal in two volumes of vapour, with the exception of those in which biatomic metals occur. Therefore, the formulæ of zinc-ethyl, zinc-methyl, mercury-methyl, mercury-ethyl, cannot be C_2H_5Zn, &c., as these formulæ only correspond to one volume of vapour, but they must be the double of that, thus:—

Zinc-methyl.	Zinc-ethyl.	Mercury-methyl.	Mercury-ethyl.
$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}Zn_2$;	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}Zn_2$;	$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}Hg_2$;	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}Hg_2$.

530. Now, if we contrast the two-volume formulæ of the hydrides and oxides of these alcohol radicals, we shall see that the metals which have hitherto been considered as the strict representatives of hydrogen, do not, as regards their state of condensation in these organo-metallic bodies, represent hydrogen; mercury and zinc represent oxygen.

Hydride of methyl.	Hydride of ethyl.	Methyl-ether.	Ethyl-ether.
H, CH_3	H, C_2H_5	$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$

531. Nor is this difference between the condensation of hydrogen and the metals confined to organic compounds. Deville and others have recently taken the vapour-density of various metallic chlorides, and have found that these likewise are present in a more condensed form than their hydrogen representative. Whereas the formula of hydrochloric acid is $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$, the formula of an equal volume of metallic choride is $\left.\begin{matrix}M_2\\Cl_2\end{matrix}\right\}$ or $\left.\begin{matrix}M_4\\Cl_4\end{matrix}\right\}$ &c.

532. From these considerations, Wanklyn and Wurtz have suggested that the equivalents of zinc, mercury, tin,

should be doubled; the equivalents of these bodies would then become $Zn=66$; $Hg=200$; $Sn=118$.*

We have already noticed (198 and 208) the way these compounds of metals and organic radicals are prepared.†

NEGATIVE GROUP.

Biatomic non-metallic elements.

$$O' \big\} O'; \quad S' \big\} S'; \quad Se' \big\} Se'; \quad Te' \big\} Te'.$$

533. The hydrogen compounds of these biatomic non-metallic elements are constructed on the type of water, and they are, therefore, noticed under that type.

Aldehydes of the bibasic mineral acids.

Hydrosulphuric acid, or aldehyde of hyposulphurous acid - - - - - -	H_2S
Hydroselenic acid, or aldehyde of hyposelenious acid - - - - - -	H_2Se
Aldehyde of sulphurous acid (not yet discovered)	H_2SO
Aldehyde of sulphuric acid (not yet discovered)	H_2SO_2

TREBLE MOLECULE.

H_3, H_3.

POSITIVE GROUP.

HYDRIDES OF METALS (PRIMARY DERIVATIVES).
METALS PROPER (SECONDARY DERIVATIVES).

534. *Primary derivatives.*—The hydrides of arsenic and antimony are constructed on the type ammonia, and therefore they are considered under that type.

535. *Secondary derivatives.*—Several metals can replace hydrogen by interchange of one atom of metal for three atoms of hydrogen; these metals are principally arsenic, antimony, bismuth, molybdenum, vanadium, tungsten,

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* See Appendix B, page 279.

† Than and Wanklyn have attempted, but hitherto without success, to form combinations of the metals with the biatomic radicals of the olefiant gas series. When they acted upon iodide of ethylene with zinc and other metals, an iodide of the metal was formed, and olefiant gas evolved. The student is referred, for further information, to their paper in the *Quarterly Journal of the Chemical Society*, vol. xii. page 258.

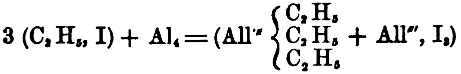
and gold; gold is the only metal of this group which is known to act sometimes as a monatomic metal. Arsenic, antimony, and bismuth will be noticed again under the negative group, and the others, with the exception of gold, on account of their rarity may be disregarded. The symbol for the molecule of gold constructed on the treble type will be Au''', Au'''.

536. Many metals can replace hydrogen by interchange of two atoms of metal for three atoms of hydrogen; "the principal metals which have this property are aluminum, cerium, uranium, chromium, iron, manganese, nickel, and cobalt, in which last two, however, the tendency is but slight. Aluminum alone is not known to replace hydrogen in any other than the above proportion. The other metals form proto, as well as sesqui-compounds. It is sometimes convenient to replace the double atom of metal in sesqui-compounds, by doubling one of the letters of its symbol, thus:—All, Ffe, Mmn, Uu, Ccr, &c., instead of Al_2, Fe_2, Mn_2, U_2, Ce_2, &c. The property which these double or twin atoms have of replacing three atoms of hydrogen, may then be conveniently indicated by the use of three dashes placed to the right of the symbols, thus:—Ffe''', All''', &c." The symbol of the molecule would then be thus expressed:—

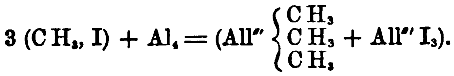
Ffe''', Ffe'''; All''', All'''; Ccr''', Ccr'''.

COMPOUNDS OF TRIATOMIC METALS WITH MONATOMIC RADICALS.

537. Aluminum treated with iodide of ethyl or iodide of methyl yields, at temperatures from 100° to 130° C., double compounds, aluminum-ethyl and iodide of ethyl, or aluminum-methyl and iodide of methyl; the organo-aluminum bodies have not yet been obtained with certainty free from iodide of aluminum. The following are the reactions:—



$$3\,(C_2H_5,\,I) + Al_4 = \left(All''' \left\{\begin{matrix} C_2H_5 \\ C_2H_5 \\ C_2H_5 \end{matrix}\right. + All''',\,I_3\right)$$



$$3\,(C\,H_3,\,I) + Al_4 = \left(All''' \left\{\begin{matrix} C\,H_3 \\ C\,H_3 \\ C\,H_3 \end{matrix}\right. + All'''\,I_3\right).$$

NEGATIVE GROUP.

HYDRIDES OF NEGATIVE OR ACID METALS (PRIMARY DERIVATIVES). SECONDARY DERIVATIVES.

538. *Primary derivatives.*—Arsenic, antimony, phosphorus, and nitrogen form terhydrides, which distinguishes them from all other elements; bismuth, which is, like arsenic, &c., a triatomic element, does not appear to form a hydride, but it forms, like the other triatomic elements, a terchloride. The following are the hydrides of this group,—ammonia, which is one of the hydrides, is a typical body, and the other three hydrides are considered to be formed on the ammonia type; they will, therefore, all be considered under the type ammonia. The following are the symbols for these molecules:—

$$H_3, N'''; H_3, P'''; H_3, As'''; H_3\,Sb'''.$$

539. The combinations of the organic radicals with nitrogen, phosphorus, arsenic, and antimony will also be considered under the ammonia type.

QUADRUPLE MOLECULE.

$$H_4, H_4.$$

540. The members of the silicon group (pp. 165 and 168) are tetratomic bodies; two of them, tin and titanium, sometimes act, as we have noticed, as biatomic elements; carbon and silicon form hydrides; marsh gas, which we have previously placed amongst the hydrides of the alcohol radicals as the hydride of methyl, may also be formulated on the quadruple molecule thus, $H_4\,C$. The composition of silicide of hydrogen has not been ascertained; but it is obtained by the action of hydrochloric acid on silicide of magnesium, and as the composition of this silicide is $Mg_4\,Si$, we may infer that the hydrogen compound is $H_4\,Si$.

APPENDIX A.

Homologous bodies.—The term homologous, which was first employed by Gerhardt, is applied to a series of analogous substances which fulfil the same chemical functions, follow the same laws of metamorphosis, and contain in their molecule *n* times CH_2, more or less. The decomposition products of homologous bodies, when these bodies are decomposed by the same agents and under the same circumstances, are also homologous.

Isologous bodies.—Bodies are termed isologous when they belong to different groups of the same class of bodies. Bodies, although allied in properties, are placed in different groups of the same class, if they differ in chemical composition. For example, the student will find that there are different groups of hydrides of alcohol radicals—different groups of alcohols; the members of the same group are homologous—the members of different groups of the same class of bodies are isologous. Example :—

Methylic alcohol is an homologue of vinic alcohol, for they differ *n* times CH_2 in their composition, and one general formula will express the composition of both bodies, thus :—

Methylic alcohol.	Vinic alcohol.	General formula.
$\left.\begin{matrix}CH_3\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_nH_{2n+1}\\H\end{matrix}\right\}O.$

But benzoic alcohol is not an homologue, but an isologue. It belongs to a different, not to the same, group of alcohols to which vinic and methylic alcohol belong, for it does not differ *n* times CH_2 in its composition, and one general formula could not express the composition of these different alcohols.

Benzoic alcohol.	General formula for the alcohols belonging to the benzoic group.
$\left.\begin{matrix}C_7H_7\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_nH_{2n-7}\\H\end{matrix}\right\}O$

APPENDIX B.

We shall here give a further quotation from Dr. Wolcott Gibbs's excellent paper on the atomic weights of the elements :—

If we admit that the molecules of all substances occupy two volumes in the gaseous state, and if the reasoning which has led chemists to double the old atomic weights of carbon, oxygen, sulphur, &c., be correct, it follows that the atomic weights of the greater number of the elements must be doubled. For we find,—

1. That nearly all volatile inorganic oxides, chlorides, oxychlorides, &c., contain, in two volumes of vapour ($H = 1$), two or four received equivalents of metal or radical. Thus the compounds whose formulæ are now usually written $Si\,Cl_2$, $Ti\,Cl_2$, $Z\,Cl_2$, $Sn\,Cl_2$, $Hg\,Cl$, $Hg_2\,Cl$, $Hg\,Br$, $Hg_2\,Br$, $Fe_2\,Cl_3$, $Al_2\,Cl_3$, $Al_2\,I_3$, $Al_2\,Br_3$, $Cr\,O_2\,Cl$, must be written $Si_2\,Cl_4$, $Ti_2\,Cl_4$, $Z_2\,Cl_4$, $Sn_2\,Cl_4$, $Hg_2\,Cl_2$, $Hg_4\,Cl_2$, $Hg_2\,Br_2$, $Hg_2\,I_2$, $Fe_4\,Cl_6$, $Al_4\,Cl_6$, $Al_4\,I_6$, $Al_4\,Br_6$, $Cr_2\,O_4\,Cl_2$, in order to correspond to two volumes of vapour.

2. All volatile metals and metallic oxides contain two or four received equivalents in two volumes of vapour. Thus the vapour-densities of mercury and cadmium represent the molecular weights, Hg_2, Cd_2. Arsenious and osmic acids correspond, in the form of vapour, to the formulæ $As_2\,O_6$ and $Os_2\,O_8$.

3. All volatile compounds of metals with organic radicals contain an even number of equivalents of metal in two volumes of vapour, excepting only those in which triatomic metals occur. Thus we have, corresponding to two volumes of vapour, the formulæ,—

$$\left.\begin{matrix} C_2\,H_3 \\ C_2\,H_3 \end{matrix}\right\}Zn_2 \quad \left.\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\}Zn_2 \quad (C_2\,H_3)_4\,Sn_2 \quad (C_4\,H_5)_4\,Sn_2$$

$$\left.\begin{matrix} (C_2\,H_3)_2 \\ (C_4\,H_5)_2 \end{matrix}\right\}Sn_2 \quad \left.\begin{matrix} (C_4\,H_5)_3 \\ Cl \end{matrix}\right\}Sn_2 \quad \left.\begin{matrix} (C_4\,H_5)_2 \\ Cl_2 \end{matrix}\right\}Sn_2 \quad \left.\begin{matrix} (C_4\,H_5)_2 \\ Br_2 \end{matrix}\right\}Sn_2$$

$$\left.\begin{matrix} (C_4\,H_5)_3 \\ Br \end{matrix}\right\}Sn_2$$

4. The volatile compounds of the triatomic radicals, nitrogen, arsenic, antimony, bismuth, and boron, contain in two volumes of vapour only one received atomic weight of the radical. Thus we have the compounds :—

$N\,H_3$, $P\,Cl_3$, $As\,Cl_3$, $Sb\,Cl_3$, $Bi\,Cl_3$, $B\,Cl_3$, $P\,(C_4\,H_5)_3$, $As\,(C_4\,H_5)_3$, $Sb\,(C_4\,H_5)_3$, $B\,(C_4\,H_5)_3$, $B\,O_3$, $3\,C_4\,H_5\,O$, &c., &c.

To this there are exceptions. Thus we have, corresponding to two volumes, the formulæ,—

$$As_2\,O_6, \left.\begin{matrix} (C_2\,H_3)_2 \\ (C_2\,H_3)_2 \end{matrix}\right\}As_2, \left.\begin{matrix} (C_2\,H_3)_2 \\ (C_2\,H_3)_2 \end{matrix}\right\}As_2\,O_2, \left.\begin{matrix} (C_2\,H_3)_2 \\ (C_2\,H_3)_2 \end{matrix}\right\}As_2\,S_2.$$

5. The specific heats of the atoms of nearly all the

elements are equal, if the molecule is in each case referred to 2 volumes of vapour.*

If, now, we consider it proved, from the above considerations, that the molecular weights of carbon, silicon, tin, titanium, and zirconium, correspond in the gaseous form to two volumes, and that these elements are tetratomic, it follows from analogy that certain other elements are also tetratomic, and we have the group,—

Carbon	12	1·68	Lead	208	6·52
Silicon	28	—	Palladium	108	6·40
Zirconium	44	—	Rhodium	102	5·62
Titanium	48	—	Ruthenium	106	—
Niobium	96	—	Platinum	198	6·40
Tantalum	136	—	Iridium	196	7·00
Tin	116	6·52	Osmium	194	5·92

The first column of numbers giving the atomic weights; the second the atomic heats, or the products of the atomic weights into the specific heats. It is possible that thorium belongs to the tetratomic group, as thoria appears to be isomorphous with stannic acid, Sn_2O_4. Lead is placed in this group from the analogy of the compounds which it forms with ethyl, methyl, &c., to stan-methyl, &c. It appears, however, like tin, palladium, ruthenium, platinum, rhodium, iridium, and osmium, to be also diatomic; the so-called protoxides having the formulæ Pb_2O_2, Sn_2O_2, &c. For similar reasons we admit the existence of six triatomic elements, namely:—

Nitrogen	14	—	Antimony	120	6·11
Phosphorus	31	5·85	Bismuth	208	6·41
Arsenic	75	6·10	Boron	11	—

The diatomic elements, according to the reasoning above mentioned, will be thirty in number, and may be arranged in natural families, as follows:—

Oxygen	16	—	Magnesium	24	—
Sulphur	32	6·48	Calcium	40	—
Selenium	80	6·08	Strontium	88	—
Tellurium	128	6·08	Barium	136	—

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* The only exception to this law occurs in the case of carbon, and cannot at present be explained.

Cerium	92	—	Chromium	52	—
Lanthanum	94	—	Aluminum	27·5	5·88
Didymium	96	—	Zinc	65·	6·24
Yttrium	—	—	Cadmium	112	6·36
Erbium	—	—	Copper	63	6·04
Terbium	—	—	Uranium	120	—
Glucinum	10	—	Mercury	200	6·40
Thorium (?)	118	—		——	
Iron	56	6·38	Molybdenum	96	6·91
Manganese	54	—	Tungsten	184	6·67
Cobalt	60	6·42	Vanadium	138	—
Nickel	58	6·28		——	

This classification into natural families appears to me to represent the present state of our knowledge, though the position of several elements must be regarded as doubtful.* The monatomic elements are only ten in number. They may be arranged in three groups:—

Chlorine,	35·5	—	Hydrogen,	1	—	Silver,	108	6·16
Bromine,	80	6·74	Lithium	7	—	Gold,	197	6·38
Iodine,	127	6·88	Sodium,	23	6·71			
Fluorine,	19	—	Potassium,	39	6·60			

It is, however, to be remarked, that, of the other elements, at least two—namely, copper and mercury—are monatomic in certain combinations, as, for example, in Cu_2Cl and Hg_2Cl. It is true that we may write these formulæ Cu_4Cl_2, and Hg_4Cl_2, in which case we have two additional diatomic forms of copper and mercury, with the atomic weights 126 and 400 respectively. This mode of viewing the subject obliges us to admit atomic heats, represented nearly by the number 12, or twice as high as in the case of the other elements, and appears, therefore, less simple than that first stated.

In like manner, all the elements belonging to the tetratomic group which form protoxides, &c., may be regarded as tetratomic and diatomic; this will add at least eight to the number of diatomic elements. Finally, in the sesquioxides, and similar compounds, two received atoms of iron, manganese, chromium, aluminum, &c., must be regarded as forming a single triatomic atom. Limpricht and Frankland admit the existence of pentatomic elements, including the nitrogen group in this class; but this view is not generally adopted, and in the present state of our knowledge, a primary division of the 60 elements into four classes, the monatomic, diatomic, triatomic, and tetratomic elements, appears to be sufficient.

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* There is reason to believe that vanadium belongs, with boron, to the nitrogen group.

From the above it appears that of the sixty elements now known to chemists, the received atomic weights of fifty at least must be doubled, if we admit the correctness of the reasoning which has led many chemists at the present day to double the atomic weights of carbon, oxygen, and sulphur. Wanklyn and Wurtz have already suggested the propriety of doubling the equivalents of zinc and tin, and, by analogy, of several other metals, while Cannizzaro has adduced the specific heats of the atoms, with other arguments, in favour of the same change. Wurtz compares oxide of zinc, Zn_2O_2, with oxide of ethylene $(C_4H_4)O_2$; the hydrate of oxide of zinc will then correspond to glycol, $\left.\begin{matrix}Zn_2\\H_2\end{matrix}\right\}O_4$. In the same way we may consider hydrate of sesquioxide of iron as corresponding to glycerine, $\left.\begin{matrix}\overset{\prime\prime}{Fe}_2\\H_3\end{matrix}\right\}O_6$ to $\left.\begin{matrix}C''_6H_5\\H_3\end{matrix}\right\}O_6$, Fe_2 being here triatomic.

Should the further progress of the science show that the views above mentioned are the most simple and consistent expression of all these facts, it will be desirable to return to the notation of Berzelius slightly modified, that is to say, it will be better to halve the atomic weights of hydrogen, and the other monatomic and triatomic elements, and denote the atomic weights of carbon, oxygen, sulphur, zinc, &c., by the numbers 6, 8, 16, 32, 5, &c., respectively. In this manner, while the formulæ are written with precisely the notation of the new school, the numbers actually employed in the great majority of calculations will be those which have been sanctioned by longest usage, and which are most convenient for practical purposes. The atomic weights of hydrogen, chlorine, potassium, and the other monatomic elements, will be in each case one-half of the old equivalent, while the molecular weights will correspond with the old equivalents. Thus we shall have,—

Hydrogen -	½	1	Oxygen -	8	16
Chlorine -	17·75	35·5	Carbon -	6	12
Bromine -	40	80	Zinc -	32·5	65
Potassium -	19·5	39	Iron -	28	56
Nitrogen -	7	14	&c.	&c.	&c.

In which table the first column gives the atomic, and the second the molecular weights.

The formula of water thus becomes H_2O, and its atomic weight 9; caustic potash is $\left.\begin{matrix}K\\H\end{matrix}\right\}O$, and its atomic weight 28; oxide of zinc will be $Zn\,O$, and its atomic weight 40·5; chlorhydric acid will be $H\,Cl$, and its atomic weight 18·25. The dashed symbols ~~H~~, ~~Cl~~, ~~K~~, &c., &c., may also be employed as in the Berzelian notation, and would in many cases be extremely convenient.

All the typical formulæ now so generally employed will be written as at present, the actual weights only being changed. The general acceptance of the views of the new school would be greatly facilitated by the adoption of the system of atomic weights here proposed.*

CHAPTER VIII.

WATER TYPE.

541. The substances treated under the simple and complex molecules are subdivided into two groups,—the positive and negative.

SIMPLE MOLECULE.

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O.$$

POSITIVE GROUP.

542. This group embraces—(1) the metallic derivatives of water; (2) the basic derivatives of ammonia, constructed on the water type; (3) the alcohols and ethers.

(1.) HYDRATES OF THE METALS PROPER (PRIMARY DERIVATIVES). ANHYDROUS OXIDES (SECONDARY DERIVATIVES).

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* *American Journal of Science and Art*, vol. xxxi. No. 92.

543. *Primary derivatives.* When one-half the hydrogen in water is replaced by a positive metal, the hydrated base or the primary derivative is produced. The semiatomic metals replace the hydrogen of the water in the proportion of two equivalents of the metal for every one of hydrogen; the hydrates of these semiatomic metals are formed on the type of a single molecule of water; their general formula is therefore $\left.\begin{matrix}M_2\\H\end{matrix}\right\}O$.

544. All those metals which we have given, under the simple molecule of hydrogen, as monatomic, form hydrates on the type of a single molecule of water; their general formula is therefore $\left.\begin{matrix}M\\H\end{matrix}\right\}O$.

545. *Secondary derivatives.*—When all the hydrogen in water is replaced by a metal, then we get the anhydrous oxides of the metals, or the secondary derivatives. The general formula of the anhydrous oxides of the semiatomic metals is $\left.\begin{matrix}M_2\\M_2\end{matrix}\right\}O$, and the general formula of the anhydrous oxides of the monatomic metals is $\left.\begin{matrix}M\\M\end{matrix}\right\}O$, as the dinoxides and the protoxides are each formed on the type of a single molecule of water.

546. The sulphides, the selenides, and tellurides, are constructed on the water type, in which the oxygen is replaced by sulphur, selenium, and tellurium; the formula of sulphide of hydrogen is therefore $\left.\begin{matrix}H\\H\end{matrix}\right\}S$, the general formula of the primary derivatives, or hydro-sulphurets, on the simple molecule, is $\left.\begin{matrix}M\\H\end{matrix}\right\}S$, and the sulphides, or secondary derivatives, is $\left.\begin{matrix}M\\M\end{matrix}\right\}S$.

EXERCISE.

134. Write out the formula for hydrate of strontium, for the protoxide of barium, for the hydrosulphuret of potassium, for the dinoxide of mercury, for the selenide of sodium, for the telluride of calcium, for the sulphide of sodium.

(2.) BASIC DERIVATIVES OF AMMONIA, CONSTRUCTED ON THE WATER TYPE.*

547. Ammonia (NH_3), when dissolved in water, is supposed to combine with an atom of water, and to become converted by this combination into a body constructed on the water type, in which one-half of the typical hydrogen has been replaced by an hypothetical compound, called ammonium; example, $\left.\begin{matrix}H_4N\\H\end{matrix}\right\}O$. (See pars. 398 to 403.) The primary, secondary, and tertiary amides are also supposed to combine, when dissolved in water, with an atom of that body, and to become converted by the combination into bodies constructed on the water type, in which one-half the typical hydrogen is replaced by complex ammoniums. Examples:—

Hydrated oxide of ethyl-ammonium.	Hydrated oxide of diethyl-ammonium.	Hydrated oxide of triethyl-ammonium.
$\left.\begin{matrix}(C_2H_5)H_3N\\H\end{matrix}\right\}O.$	$\left.\begin{matrix}(C_2H_5)_2H_2N\\H\end{matrix}\right\}O.$	$\left.\begin{matrix}(C_2H_5)_3HN\\H\end{matrix}\right\}O.$

548. As the ammonia escapes, like hydrochloric acid gas, from its aqueous solution at common temperatures, a solution of ammonia in water would appear to be, like a solution of hydrochloric acid gas in water, merely a mechanical solution, no combination taking place, especially as its odour and other properties are unaffected by the solution; and that it cannot, therefore, become changed by its solution into a body constructed on another type. The same objections might be urged against the assumption that the primary, secondary, and tertiary monamines become changed into bodies formed on the water type when they are dissolved in water, as the volatility, &c., of these monamines are little, if at all, affected by their solution in water. But these doubts cannot be extended to the tetra-compound-ammoniums, as in these bodies the fourth atom of the hydrogen in the ammonium has been replaced by another radical, thus—$\left.\begin{matrix}(C_2H_5)_4N\\H\end{matrix}\right\}O$. In these tetra-compounds, the odour and volatility of the hydrated oxides of ammonium, ethyl,

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[*] This group of basic derivatives of ammonia must be passed over, and not entered upon until the student has gone over the monamines, monamides, and the haloid combinations of the monammoniums.

diethyl and triethyl-ammonium, have entirely disappeared; they more resemble caustic potash in their chemical characters than they resemble ammonium, or the other ammonium derivatives; like potash, they liberate ammonia from its combinations; like it, they are highly caustic, deliquesce, and rapidly attract carbonic acid from the air; they saponify fats; their solutions resemble the solution of caustic potash so perfectly that they might easily be mistaken for that substance by their chemical reactions. The solubility in water of these different ammonia derivatives does not follow in the order of their substitution, the tetra-compounds forming the exception. For instance, ethylamine is almost as soluble in water as ammonia; diethylamine is less soluble; triethylamine is still less soluble, whilst the hydrate of tetrethylammonium is so extremely soluble in water that it dissolves in all proportions in that liquid.

549. The hydrates of these tetra-compound ammoniums are obtained, as we have seen, by digesting oxide of silver in a solution of their iodides, these hydrates and iodide of silver being formed. They can also be prepared, but not so advantageously, by decomposing their sulphates by baryta water.

550. Their oxygen salts can be obtained by digesting the iodides on a corresponding silver salt; for instance, if we wish to prepare their sulphates, we may digest the iodides on sulphate of silver. They can also be prepared by adding the hydrated oxides of these bases and the acids together.

551. These hydrated tetra-compounds are decomposed by heat; they split up into the corresponding tertiary amine and other products; the ethyl-compound is decomposed into triethylamine, olefiant gas, and water; ethyl is the radical which is always decomposed, whether it is mixed with methyl, amyl, or phenyl, and it is always decomposed into olefiant gas. The amyl-compound is decomposed into triamylamine, amylene and water. The methyl-compound is decomposed into trimethylamine and methyl-alcohol.

EXERCISES.

135. Write out the formula of hydrated oxide of tetrethylammonium, of tetramylammonium, of tetrallylammo-

nium, of methyl-triethylammonium, of trimethyl-vinylammonium, of methyl-diethyl-phenylammonium, of methyl-diethyl-phenylammonium, of methyl-ethyl-amyl-phenyl-ammonium, of diethyl-piperyl-ammonium, of diethyl-conyl-ammonium, of ethyl-picolyl-ammonium, of methyl-leucolyl-ammonium, of methyl-morphyl-ammonium, of ethyl-codeyl-ammonium; and state how you would prepare their different bases.

136. What decomposition will the hydrated oxide of methyl-ethyl-amyl-phenylammonium undergo when heated?

Phosphoniums, Arseniums, Stiboniums.

552. The phosphines, arsenines, and stibines, are converted into the iodides of the *onium* compounds by simply treating them with the bromides or iodides of the alcohol radicals; and from the bromides or iodides thus formed the hydrated oxides are prepared by digesting them in oxide of silver. These hydrates form strong alkaline solutions.

EXERCISE.

137. Write out the formula of hydrated oxide of tetrethyl-stibonium, of tetramethyl-arsonium, and of tetrethyl-phosphonium.

(3.) Alcohols and Ethers.

553. *The bodies termed alcohols defined.*—The term alcohol is now applied to all bodies in which one-half the hydrogen in *one, two, three,* &c., atoms of water is replaced by a basic radical, composed of carbon and hydrogen. When the basic radical replaces only one equivalent of hydrogen it is called a monatomic or uniatomic radical; when it replaces two atoms it is called a diatomic or biatomic radical; when it replaces three atoms it is called a teratomic or triatomic radical; the radicals are called by the general term polyatomic when they can replace more than one equivalent of hydrogen.

554. *The bodies termed ethers defined.*—When all the hydrogen in one, two, three, &c., atoms of water is replaced by the same or different alcoholic radicals, such bodies are termed ethers; therefore the ethers stand in the same relation to the alcohols as the anhydrous inorganic bases stand to their hydrates. Examples:—

Anhydrous potash.	Hydrate of potash.	Vinic ether.	Vinic alcohol.
$\left.\begin{matrix}K\\K\end{matrix}\right\}O.$	$\left.\begin{matrix}K\\H\end{matrix}\right\}O.$	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O.$	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O.$

555. The alcohols are therefore termed the *primary derivatives;* the ethers are termed the *secondary derivatives.* When the hydrogen acids are added to the alcohols, the radicals in the alcohols combine, like the metals, with the electro-negative element of the acids, forming haloid combinations, which are frequently called *simple ethers.* When the oxygen acids are added to the alcohols, the oxides of the alcohol radicals combine, like the metallic oxides, with the acids, forming salts, which are frequently termed *compound ethers.*

ALCOHOLS CONTAINING MONATOMIC RADICALS.

556. There are five groups or classes already known of monatomic alcohols; the general formula of the first class, which contains at present most members, is $\left.\begin{matrix}C_nH_{2n+1}\\H\end{matrix}\right\}O$; the general formula of the second class is $\left.\begin{matrix}C_nH_{2n-1}\\H\end{matrix}\right\}O$; the general formula of the third class is $\left.\begin{matrix}C_nH_{2n-7}\\H\end{matrix}\right\}O$; the general formula of the fourth is $\left.\begin{matrix}C_nH_{2n-9}\\H\end{matrix}\right\}O$; and the general formula of the fifth is $\left.\begin{matrix}C_nH_{2n-6}\\H\end{matrix}\right\}O$.

FIRST CLASS OF ALCOHOLS AND ETHERS.

(*General formula for the alcohols,* $\left.\begin{matrix}C_nH_{2n+1}\\H\end{matrix}\right\}O$.)

557. We have shown that alcohol is now employed as a generic term, that is, that it is applied to a group of bodies; but it was in the first instance applied exclusively to the volatile inflammable body which is produced by the ordinary fermentation of sugar.

558. The following is a list of the alcohols at present known belonging to this group, but it is beyond a doubt that the list ought to be extended, and no doubt will be, as the science progresses.

559. The student must commit to memory the names and symbols of these alcohols.

Names.		Formulæ.	Specific Gravity.		Boiling point, F.
			Liquid.	Vapour.	
Methylic alcohol (wood spirit) - - - -	Liquid	$\left.\begin{matrix}C\,H_3\\H\end{matrix}\right\}O$	0·798	1·12	149·9
Ethylic alcohol (spirit of wine) - - - -	”	$\left.\begin{matrix}C_2\,H_5\\H\end{matrix}\right\}O$	0·7938	1·6133	173
Propylic or tritylic alcohol	”	$\left.\begin{matrix}C_3\,H_7\\H\end{matrix}\right\}O$	. .	2·02	206
Butylic or tetrylic alcohol	”	$\left.\begin{matrix}C_4\,H_9\\H\end{matrix}\right\}O$	. .	. .	233
Amylic alcohol (fousel oil)	”	$\left.\begin{matrix}C_5\,H_{11}\\H\end{matrix}\right\}O$	0·8184	3·147	269·8
Caproic or hexylic alcohol	”	$\left.\begin{matrix}C_6\,H_{13}\\H\end{matrix}\right\}O$	0·833	3·53	299-309
Caprylic or octylic alcohol	”	$\left.\begin{matrix}C_8\,H_{17}\\H\end{matrix}\right\}O$	0·823	4·5	356
Cetylic alcohol (ethal) -	Solid	$\left.\begin{matrix}C_{16}\,H_{33}\\H\end{matrix}\right\}O$			
Cerylic alcohol - - -	”	$\left.\begin{matrix}C_{27}\,H_{55}\\H\end{matrix}\right\}O$			
Melissic alcohol - -	”	$\left.\begin{matrix}C_{30}\,H_{61}\\H\end{matrix}\right\}O$			

560. "The first of these liquids is found among the products of the destructive distillation of wood; the second, third, fourth, and fifth, are formed by the fermentation of saccharine substances; caprylic alcohol is obtained by saponifying castor oil with hydrate of potash, and distilling the product with excess of the alkali at a high temperature; cetylic alcohol is obtained from spermaceti; cerylic alcohol from Chinese wax, and melissic alcohol from beeswax."

561. Wanklyn and Erlenmeyer have very recently obtained hexylic alcohol by a very interesting decomposition; viz., by the action of hydriodic acid upon mannite; they state that this latter body may be regarded as a six-atomic alcohol, or better as *hydride of hexyl,* in which six atoms of hydrogen are replaced by six atoms of peroxide of hydrogen.

$$\text{Mannite} = C_6\,H_8\,(H\,O)_6.$$

This formula, they state, is established by the reaction between mannite and hydriodic acid. When the two bodies are heated together, iodine is evolved, and a heavy, oily liquid distils; this liquid is iodide of hexyl ($C_6\,H_{13}\,I$).

$$C_6\,H_8\,(H\,O)_6 + 11\,H\,I = C_6\,H_{13}\,I + 6\,H_2O + 10\,I.$$

If the iodide is digested with water and oxide of silver, hexylic alcohol is obtained. When caustic potash and vinic alcohol are employed, instead of oxide of silver and water, a different result occurs. The iodide splits up into hexylene and hydriodic acid, which latter, of course, acts upon the potash.*

562. These alcohols are homologous bodies, as they differ from one another by $n\,C\,H_2$: as the caprylic differs from the next lowest yet discovered, viz., caproic, by $C_2\,H_4$, or $2\,C\,H_2$, it shows that there is a member missing of this composition, $\left.\begin{matrix}C_7\,H_{15}\\H\end{matrix}\right\}O$. The other gaps in the series point out the absence of other members, as each member differs from the next above it (if that has been discovered), or the next lowest (if that has been discovered), by a difference of $C\,H_2$. The boiling point of these homologous bodies, it will be observed, rises with each additional increment of $C\,H_2$ by about 33° F. All, except some of the higher members, are capable of being distilled without decomposition.

563. By the action of oxidizing agents, the alcohols pass first into a heterologous or collateral series of bodies termed aldehydes (478), and these pass into a collateral series of acids, thus:—

$$\overset{\textbf{Alcohols}}{\left.\begin{matrix}C_n\,H_{2n+1}\\H\end{matrix}\right\}}O+O=\overset{\textbf{Aldehydes.}}{\left.\begin{matrix}C_n\,H_{2n-1}O\\H\end{matrix}\right\}}+\left.\begin{matrix}H\\H\end{matrix}\right\}O$$

and—

$$\overset{\textbf{Aldehydes.}}{\left.\begin{matrix}C_n\,H_{2n-1}O\\H\end{matrix}\right\}}+O=\overset{\textbf{Acids.}}{C_n\,H_{2n-1}\left.\begin{matrix}O\\H\end{matrix}\right\}}O$$

These acids will come under our consideration in the negative series.

564. We must, before proceeding further, explain the meaning of heterologous series. "Every compound in a homologous series, when subjected to the action of chemical reagents, furnishes other compounds, differing in compo-

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* We direct the student's attention to the action of hydriodic acid. It has only been recently introduced into organic chemistry as a deoxidizing agent, which its ready decomposition enables it so well to fulfil. Its action upon lactic, malic, and tartaric acids, and upon other bodies, has been attended with important and interesting results, as the student will hereafter learn.

sition from those from which they are obtained, but yet bearing a definite relation to them. Thus alcohol yields, under various circumstances, ether, aldehyde, acetic acid, &c.; and these *heterologous* or differently constituted bodies belong to collateral, and intimately related, but different series; for it is found that the different members of a homologous series exhibit an analogous deportment when submitted to similar chemical reagents, and furnish derivative series in which the homology is still preserved."

565. *Substitution of the typical hydrogen*[*] *in the alcohols by other radicals.*—The typical hydrogen in the alcohols can be replaced—(1) By an atom of the alcohol radicals: the ethers are produced by this substitution. (2) By the radicals of the oxygen acids. Example:—

Chloride of benzoyl.

$$\left.\begin{matrix}C_nH_{2n+1}\\H\end{matrix}\right\}O + C_7H_5O,Cl = \left.\begin{matrix}C_nH_{2n+1}\\C_7H_5O\end{matrix}\right\}O + HCl$$

(3) By metals.—The replacement of the hydrogen by potassium or sodium is effected by immersing the metal in absolute alcohol, hydrogen gas is evolved, and a colourless, crystallizable compound is obtained, the general formula of which is $\left.\begin{matrix}C_nH_{2n+1}\\M\end{matrix}\right\}O$. The compound obtained on treating vinic alcohol with potassium, is called ethylate of potassium. Its formula is $\left.\begin{matrix}C_2H_5\\K\end{matrix}\right\}O$.

366. *The oxygen in alcohols can be replaced by sulphur* (and, of course, selenium, tellurium, or any of the other members of the sulphur class).—We then get bodies termed *mercaptans*, whose general formula is $\left.\begin{matrix}C_nH_{2n+1}\\H\end{matrix}\right\}S$. The mercaptans may be obtained by distilling sulphide of potassium and the chloride of an alcohol radical together, or by distilling sulphide of potassium and a sulphovinate of lime, or by acting upon the alcohol with persulphide of phosphorus, thus:—

$$5\left(\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O\right) + P_2S_5 = 5\left(\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S\right) + P_2O_5.$$

567. In these sulphur-alcohols (mercaptans), as in

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[*] By typical hydrogen is meant the hydrogen of the type (water) from which the alcohols are derived.

oxygen alcohols, we can replace the atom of hydrogen by a metal; thus, by adding the oxide of lead, copper, silver, gold, or of mercury, to an alcohol solution of a mercaptan, we obtain a mercaptan with one of these metals in the place of hydrogen; on adding potassium to a mercaptan, hydrogen is evolved, and a mercaptan with potassium in the place of hydrogen is obtained.

568. *Action of oxygen on the alcohols.*—Under the influence of oxidizing agents, this class of alcohols is converted into the first class of aldehydes; and by continuing the action of the oxidizing agents, these aldehydes pass into acids, having the general formula $\left.\begin{matrix}C_n H_{2n-1} O\\ H\end{matrix}\right\} O$. This reaction, which is characteristic, serves to distinguish the different alcohols.

569. *Action of potash on the alcohols.*—Treated with potash at an elevated temperature, hydrogen is disengaged, and a potash salt of one of the acids, having the general formula $\left.\begin{matrix}C_n H_{2n-1} O\\ H\end{matrix}\right\} O$ is formed.

570. *Action of sulphuric acid.*—The alcohols dissolve in sulphuric acid, and they combine with it, forming sulphovinic acids. The general formula of these bodies is $\left.\begin{matrix}(S O_2)''\\ (C_n H_{2n+1})\\ H\end{matrix}\right\} O_2$; they are therefore bodies in which one of the two typical atoms of hydrogen in sulphuric acid has been replaced by an alcohol radical. They possess an acid reaction, and the other typical atom of hydrogen can be replaced by an alcohol radical, or by a metal. They are, in fact, compound acid ethers. We shall see hereafter that the other bibasic acids and tribasic acids form analogous compounds. This is not the only action of sulphuric acid on the alcohols.

571. *Action of some acids and salts on the alcohols.*—When alcohols are heated with sulphuric acid (not employed in excess), or with phosphoric acid, fluoride of boron, chloride of zinc, or chloride of tin, many of the alcohols give the ethers. (See par. 376.) Heated with an excess of sulphuric acid, they yield hydrocarbons of the olefiant gas series, having the general formula $C_n H_{2n}$. (See par. 522.)

572. With the hydrogen acids they give the halogen

ethers, or, as they are sometimes called, the simple ethers. Example:—

$$\left.\begin{matrix}C_n H_{2n} + \\ H\end{matrix}\right\} O + H Cl = C_n H_{2n+1} Cl + \left.\begin{matrix}H \\ H\end{matrix}\right\} O.$$

These bodies are given under the type hydrochloric acid.

First Class of Ethers.

$$\left(\textit{General formula, } \left.\begin{matrix}C_n H_{2n+1} \\ C_n H_{2n+1}\end{matrix}\right\} O. \right)$$

573. These bodies represent water in which the two atoms of hydrogen have been replaced by two equivalents of monatomic alcohol radicals. They are gaseous (methylic ether), liquid, or solid (cetylic ether); they have not any action upon vegetable colours, and are for the most part volatile, without decomposition. Their volatility is greater than that of the corresponding alcohols.

574. We have seen how they are prepared, and that they may be composed of two different alcohol radicals. When this is the case, we get what are termed mixed ethers.

575. Sulphuric acid and the hydrogen acids form with the ethers the same compounds as they form with the alcohols. Sulphuric acid forms with them, for instance, sulphovinates, and the hydrogen acids form with them the chlorides, &c., of the alcohol radicals.

576. *Sulphur can be substituted for the oxygen in ethers.*—If we act upon the chlorides of the alcohol radicals with the monosulphide of potassium, we obtain the sulphur ethers, thus:—

$$2\left(C_n H_{2n+1} Cl\right) + \left.\begin{matrix}K \\ K\end{matrix}\right\} S = \left.\begin{matrix}C_n H_{2n+1} \\ C_n H_{2n+1}\end{matrix}\right\} S + 2 K Cl.$$

They may also be prepared by acting upon the ethers with persulphide of phosphorus, thus:—

$$5\left(\left.\begin{matrix}C_n H_{2n+1} \\ C_n H_{2n+1}\end{matrix}\right\} O\right) + P_2 S_5 = 5\left(\left.\begin{matrix}C_n H_{2n+1} \\ C_n H_{2n+1}\end{matrix}\right\} S\right) + P_2 O_5$$

577. The sulphuretted ethers are fœtid oily bodies, or crystalline solids. They are insoluble in water. They do not form salts, like the mercaptans, but they precipitate bichloride of mercury, and bichloride of platinum, forming, like the mercaptans, combinations with these chlorides.

578. Chlorine can be substituted for the hydrogen in the radicals of the ethers.

EXERCISES.

138. Give the formula for sulphuretted methylic alcohol, and state how you would prepare it.

139. Give the formula for ethylate of zinc, and state how you would prepare it.

140. Give the formulæ for methylic, for ethylic, for propylic, for butylic, for amylic, for caprylic, for cetylic, ether.

141. Give the formulæ for methylate of potassium and amylate of sodium, and state how you would prepare them.

142. Give the formula for sulphuretted methylate of mercury, and state how you would prepare it.

143. Give the formulæ for methyl-amylic, for methyl-ethylic, for ethyl-amylic, ether, and state how you would prepare these different ethers.

144. Give the formulæ for sulphuretted methylic, and for sulphuretted amylic, ether, and state how you would prepare them.

Second Class of Alcohols and Ethers.

(*General formula for the alcohols,* $\left.\begin{matrix}C_nH_{2n-1}\\H\end{matrix}\right\}O.$)

579. Only one alcohol belonging to this class is yet known; this alcohol is termed allylic alcohol $\left.\begin{matrix}C_3H_5\\H\end{matrix}\right\}O$ and corresponds to the second class of hydrocarbons, aldehydes, and chlorides, of the monatomic radicals.

580. *Preparation.* — Hofmann and Cahours,* who obtained this alcohol, found that silver salts are in general powerfully attacked by iodide of allyl; but comparatively few of the products obtained in this reaction are themselves appropriate for the separation of allylic alcohol. They obtained the most satisfactory results with oxalate of allyl. They therefore prepared the allylic alcohol in the following way:—they digested for several hours, at a temperature of 100° C., iodide of allyl (C_3H_5I) upon oxalate of silver (the iodide acts very energetically

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* "Researches on a New Class of Alcohols," by Dr. A. W. Hofmann and A. Cahours. *Chemical Society's Journal,* vol. x.

upon the silver salt); at the end of that time the reaction is complete. The digestion is most conveniently accomplished in the presence of anhydrous ether. The oxalate of allyl furnished by this process can be easily purified; on filtering the etherial liquid from the iodide of silver, and distilling, the ether passes over first, the temperature then rises rapidly, and between 205° and 207° C., a colourless transparent liquid distils over, which is the oxalate of allyl $\left.\begin{matrix}(C_2O_2)''\\(C_3H_5)_2\end{matrix}\right\}O_2$. When once the oxalate of allyl has been procured, nothing is easier than to separate from it the allylic alcohol. It is only necessary to treat this product with an excess of dry ammonia, by which oxamide and the allylic alcohol are obtained, according to the following equation:—

$$\left.\begin{matrix}(C_2O_2)''\\(C_3H_5)_2\end{matrix}\right\}O_2 + 2\,H_3N = \overset{\text{Oxamide.}}{\left.\begin{matrix}(C_2O_2)''\\H_4\end{matrix}\right\}N_2} + 2\left(\left.\begin{matrix}C_3H_5\\H\end{matrix}\right\}O\right),$$

a result in perfect accordance with the reciprocal action of ammonia and oxalic ether:—

Oxalic ether.

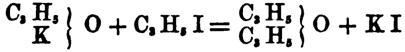
$$\left.\begin{matrix}(C_2O_2)''\\(C_2H_5)_2\end{matrix}\right\}O_2 + 2\,H_3N = \left.\begin{matrix}(C_2O_2)''\\H_4\end{matrix}\right\}N_2 + 2\left(\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}\quad\right)$$

581. The alcohol separated by distillation from the oxamide is not absolutely pure; it may retain water and ammonia: a simple rectification from anhydrous sulphate of copper is sufficient to render it perfectly pure.

582. *Properties of the alcohol.*—It is a colourless, very mobile liquid, possessing a pungent odour, recalling at the same time that of common alcohol and of mustard-oil. It boils about 100° C. and is combustible, but burns with a far more luminous flame than ordinary alcohol. Its flavour is spirituous and pungent. Water, alcohol, and wood-spirit dissolve it in all proportions.

583. *Substitution of other bodies for the typical hydrogen.*—Potassium and sodium attack allylic alcohol energetically, especially if the temperature be slightly raised; hydrogen is copiously evolved, and the potassium or sodium compound, in the form of a gelatinous substance, is produced; the formula of this substance is $\left.\begin{matrix}C_3H_5\\K\end{matrix}\right\}O$. If we treat

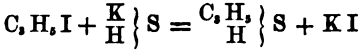
this substance with iodide of allyl, we get the ether, thus:—



$$\left.\begin{matrix}\mathrm{C_3H_5}\\ \mathrm{K}\end{matrix}\right\}\mathrm{O} + \mathrm{C_3H_5I} = \left.\begin{matrix}\mathrm{C_3H_5}\\ \mathrm{C_3H_5}\end{matrix}\right\}\mathrm{O} + \mathrm{KI}$$

If we treat methyl, ethyl, amyl, and phenyl-potassium alcohols with iodide allyl, or *vice versâ*, we obtain mixed ethers.

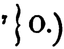
584. *Substitution of sulphur for the oxygen in the alcohol.*—When iodide of allyl is allowed to fall drop by drop into a concentrated alcoholic solution of the sulphide of hydrogen and potassium, allylic mercaptan is formed, thus:—



$$\mathrm{C_3H_5I} + \left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S} = \left.\begin{matrix}\mathrm{C_3H_5}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S} + \mathrm{KI}$$

This sulphur alcohol has the odour of garlic; it boils at 90° C.; it acts with energy upon oxide of mercury, with which it forms a compound dissolving in boiling alcohol, and separating from it on cooling, in the form of pearly scales of remarkable brilliancy, and which present the greatest resemblance to mercaptide of mercury.

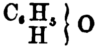
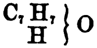
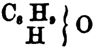
THIRD CLASS OF ALCOHOLS AND ETHERS.

(*General formula for the alcohols,*  $\left.\begin{matrix}\mathrm{C_n\,H_{n2-7}}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}$.)

585. There are two groups of alcohols having the same general formula; they are not identical or homologous, but isomeric; they are distinguished from one another by their behaviour with oxidizing agents: the bodies of the one group are not converted into aldehydes by these agents; whilst the others are converted into aldehydes by these agents.

FIRST GROUP.

586. Only three members are yet known belonging to this group; the following are their names and formulæ, which must be committed to memory:—

Phenylic alcohol, carbolic acid, hydrate of phenyl, phenol - - - -	 $\left.\begin{matrix}\mathrm{C_6H_5}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}$
Cresylic alcohol - - - - - -	 $\left.\begin{matrix}\mathrm{C_7H_7}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}$
Hydrate of oxide of xylyl - - -	 $\left.\begin{matrix}\mathrm{C_8H_9}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}$

587. These substances are found in the liquid products obtained in the dry distillation of wood, and in coal tar. Hydrate of phenyl has been the most extensively studied; its action on organic compounds is the same as that of creosote; thus it dissolves indigo, &c., and coagulates albumen, preventing the putrefaction of animal substances. Sulphur and chlorine dissolve in it; nitric acid, chlorine, and bromine attack it with energy. It is easily recognised by its action on pine-wood; if the wood be dipped first into the hydrate of phenyl, and then into moderately strong nitric acid, the wood becomes stained deep blue, which soon passes into brown.

588. *Replacement of the typical hydrogen.*—If potassium be added to phenyl-alcohol it dissolves with evolution of hydrogen, the potassium compound being produced, $\left.\begin{matrix}C_6H_5\\K\end{matrix}\right\}O$; on heating this compound with the iodides of the alcohol radicals, a series of mixed ethers are produced, thus:—

$$\left.\begin{matrix}C_6H_5\\K\end{matrix}\right\}O + CH_3I = \left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\}O + KI$$

589. *Replacement of the hydrogen in the alcohol radical by other bodies.*—Some of the hydrogen atoms in the alcohol radical have been replaced by chlorine, bromine, and NO_2, as the following list proves:—

Dichlorophenic, or chlorophenesic acid -	$\left.\begin{matrix}(C_6H_3Cl_2)\\H\end{matrix}\right\}O$
Trichlorophenic, or chlorophenisic acid -	$\left.\begin{matrix}(C_6H_2Cl_3)\\H\end{matrix}\right\}O$
Pentachlorophenic, or chlorophenusic acid	$\left.\begin{matrix}(C_6Cl_5)\\H\end{matrix}\right\}O$
Bromophenic, or bromophenasic acid -	$\left.\begin{matrix}(C_6H_4Br)\\H\end{matrix}\right\}O$
Dibromophenic, or bromophenesic acid -	$\left.\begin{matrix}(C_6H_3Br_2)\\H\end{matrix}\right\}O$
Tribromophenic, or bromophenisic acid -	$\left.\begin{matrix}(C_6H_2Br_3)\\H\end{matrix}\right\}O$
Nitrophenic, or nitrophenasic acid -	$\left.\begin{matrix}(C_6H_4NO_2)\\H\end{matrix}\right\}O$
Dinitrophenic, or nitrophenesic acid -	$\left.\begin{matrix}[C_6H_3(NO_2)_2]\\H\end{matrix}\right\}O$

Trinitrophenic, or nitrophenisic acid (carbazotic acid, or picric acid) -	$\left.\begin{matrix}[C_6H_2(NO_2)_3]\\H\end{matrix}\right\}O$
Dichloronitrophenic acid - - -	$\left.\begin{matrix}(C_6H_2Cl_2NO_2)\\H\end{matrix}\right\}O$
Diniodonitrophenic acid - - -	$\left.\begin{matrix}(C_6H_2I_2NO_2)\\H\end{matrix}\right\}O$
Bromodinitrophenic acid - -	$\left.\begin{matrix}[C_6H_2Br(NO_2)_2]\\H\end{matrix}\right\}O$

590. All of these acids are monobasic, and form definite salts, many of which crystallize very beautifully. When the nitro-acids are submitted to the reducing action of hydrosulphate of ammonia, two red amidated acids are produced. Carbazotic acid is produced not only from phenyl-alcohol by the action of nitric acid, but it is also a frequent product of the action of this acid upon complex organic substances; salicin, coumarin, phloridzin, silk, indigo, and a variety of resins yield it when treated with fuming nitric acid.

591. *Action of sulphuric acid upon phenic alcohol.*—Sulphuric acid forms with the alcohol an acid corresponding to sulphovinic acid.

592. The alcohols of this group do not give either hydrocarbons or ethers by the action of the sulphuric acid upon them.

593. *Action of ammonia upon the alcohols.*—When the alcohol is heated for some time with ammonia in sealed tubes, aniline (phenylamine) $\left.\begin{matrix}C_6H_5\\H_2\end{matrix}\right\}N$ is produced.

SECOND GROUP.

594. Only three members are yet known belonging to this group, and the last, which has only very recently been discovered by Drs. De la Rue and Müller, has been as yet only very imperfectly studied. The following are the names and formulæ of the three alcohols; they must be committed to memory:—

	Boils	
Benzoic alcohol, oily liquid	- 400° F.	- $\left.\begin{matrix}C_7H_7\\H\end{matrix}\right\}O$
Cuminic alcohol, oily liquid	- 470° F.	- $\left.\begin{matrix}C_{10}H_{13}\\H\end{matrix}\right\}O$
	Melts about	
Sycocerylic alcohol, crystalline solid - - -	194° F.	- $\left.\begin{matrix}C_{18}H_{29}\\H\end{matrix}\right\}O$

595. Benzoic and cuminic alcohols are obtained by dissolving their aldehydes in their own volume of alcohol, and subsequently mixing the alcoholic solution with an alcoholic solution of hydrate of potash. Two equivalents of the aldehyde split up into one equivalent of the corresponding alcohol and one of the corresponding acid, thus:—

$$2\,(C_7H_5O, H) + \left.\begin{matrix}K\\H\end{matrix}\right\}O = \left.\begin{matrix}C_7H_7\\H\end{matrix}\right\}O + \left.\begin{matrix}C_7H_5O\\K\end{matrix}\right\}O$$

Benzoic alcohol has also been prepared by boiling for three or four hours monochloride of toluene with acetate of potash. Acetate of the alcohol is formed, and chloride of potassium. The alcohol is afterwards separated from the acetic acid by boiling the acetate with an alcoholic solution of potash. The sycocerylic alcohol is found in combination with acetic acid in the resin of *Ficus rubiginosa.*

596. Oxidizing agents convert the first two into aldehydes and acids. When distilled from hydrate of potash, they are decomposed into the corresponding acids, and the hydrides of the alcohol radicals. The ethers are obtained by heating the alcohols in a closed vessel for some hours with anhydrous boracic acid; a hydrocarbon is formed along with the ether. When they are mixed with sulphuric acid, they yield compound acids corresponding to sulphethylic acid.

FOURTH CLASS OF ALCOHOLS.

$$\left(\textit{General formula, } \left.\begin{matrix}C_nH_{2n-9}\\H\end{matrix}\right\}O.\right)$$

597. Cinnamic alcohol (styrone, Peruvine) is the only alcohol belonging to this group which has yet been discovered. Its formula is $\left.\begin{matrix}C_9H_9\\H\end{matrix}\right\}O$. It is produced by the distillation of styracine with a concentrated solution of potash. No ether corresponding to this alcohol has yet been obtained. When exposed to the action of atmospheric air, under the influence of platinum black, it yields the corresponding aldehyde (oil of cinnamon); when acted upon by nitric acid, it yields hydride of benzoyl.

FIFTH CLASS OF ALCOHOLS.

(*General formula*, $\left.\begin{matrix}C_nH_{2n-6}\\H\end{matrix}\right\}O.$)

598. Hydride of anisyle exhibits the same behaviour as hydride of benzoyl, with an alcoholic solution of potash. It is converted into a mixture, anisate of potash, and a crystalline body, which, when purified by distillation, boils at 482° F. The formula of this body, which is anisic alcohol, is $\left.\begin{matrix}C_8H_{10}O\\H\end{matrix}\right\}O.$

EXERCISES.

145. Give the formula, and state how you would prepare sulphuretted allylic alcohol, and sulphuretted allylate of mercury.

146. Give the formula, and state how you would prepare ethyl-allylic ether.

NEGATIVE GROUP.

599. This group embraces—(1) The monobasic inorganic acids. (2) The monobasic organic acids. (3) The salts of these two classes of acids. (4) The ethers of these acids. (5) The monamidic acids and their salts.

BASICITY OF ACIDS.

600. Acids are formed on the type of water in which the hydrogen is partly or wholly replaced by the acid radical. When only part of the hydrogen in the type is replaced by the acid radical, the hydrate of the acid, or the acid proper, is obtained. When all the hydrogen in the type is replaced by the acid radical, the *acid anhydride* is produced.

601. The hydrated acids undergo double decompositions with the metallic bases, and they exchange for the metal their disposable hydrogen; the product produced by the exchange is an oxygen salt; under certain conditions, the acids also undergo double decompositions with the alcohols, compound ethers being produced. The hydrogen in the acids, which is capable of being exchanged for the radical of the bases and alcohols, is called *basic hydrogen*.

602. The acids are monatomic, biatomic, or triatomic, according as their molecule is derived from *one*, *two*, or *three* molecules of water. As the basicity of an acid depends on the number of atoms of basic hydrogen it

contains, we might expect that all biatomic acids, as they contain two atoms of typical hydrogen, would be bibasic; and that all triatomic acids, on account of their containing three atoms of typical hydrogen, would be tribasic; but we shall see hereafter that it is highly probable that each of the two or three atoms of typical hydrogen in biatomic and triatomic acids is not always or necessarily basic. We have, therefore, to make a distinction between the terms diatomic, triatomic, &c., which refer to the complication of molecules, and the terms bibasic, tribasic, &c., which refer to the capacity of saturation. All monatomic acids, as they contain only one typical atom of hydrogen, are of course monobasic.

603. "The determination of the basicity of an acid is a matter of some difficulty. In many cases, the formation or non-formation of acid and double salts may serve as a distinction. Thus, tartaric acid, which is a bibasic acid, $\left.\begin{matrix} C_4H_4O_4 \\ H_2 \end{matrix}\right\} O_2$, forms a neutral tartrate of potash, $\left.\begin{matrix} C_4H_4O_4 \\ K_2 \end{matrix}\right\} O_2$, and an acid tartrate, $\left.\begin{matrix} C_4H_4O_4 \\ KH \end{matrix}\right\} O_2$; so, likewise, sulphuric acid forms $\left.\begin{matrix} (SO)_2'' \\ K_2 \end{matrix}\right\} O_2$, and $\left.\begin{matrix} (SO)_2'' \\ KH \end{matrix}\right\} O_2$; whereas, nitric acid, having but one atom of hydrogen, forms but one potash salt, viz., $\left.\begin{matrix} NO_2 \\ K \end{matrix}\right\} O$. But acetic acid, generally regarded as monobasic, $\left.\begin{matrix} C_2H_3O \\ H \end{matrix}\right\} O$, also forms not only a neutral potash salt, $\left.\begin{matrix} C_2H_3O \\ K \end{matrix}\right\} O$, but likewise an acid potash salt, usually represented by the formula, $C_2H_3KO_2 \, . \, C_2H_4O_2$; but if the formula of acetic acid be doubled, making $C_4H_8O_4$, the neutral potash salt will be $C_4H_6K_2O_4$, and the acid salt $C_4H_6(KH)O_4$. Acetic acid will thus be represented as a bibasic acid; and, in fact, this quantity, $C_4H_8O_4$ (= 120), is the equivalent of sulphuric acid, SH_2O_4 (= 98), that is to say, it saturates the same quantity of potash. Why, then, is acetic acid universally regarded as monobasic? On this point we shall quote the observations of Gerhardt:—

604. "The basicity of acids is a question, not of equivalents, but of molecules. . . If we examine, *under the same volume*, the composition of the vapour of certain volatile

bodies, corresponding to the acids, and compare together the similar terms, such as the chlorides of the acid radicals, or the neutral compound ethers, we observe perfectly regular differences, which are always related to the chemical properties of the corresponding bodies; thus,—

$$2\text{ volumes of}\begin{cases}\text{chloride of acetyl contain} & - \; Cl, C_2H_3O\\ \text{chloride of sulphuryl ,,} & - \; Cl_2, SO_2\end{cases}$$

$$2\text{ volumes of}\begin{cases}\text{acetate of methyl contain} & - \; \left.\begin{matrix}C_2H_3O\\ CH_3\end{matrix}\right\}O\\ \text{sulphate of methyl ,,} & - \; \left.\begin{matrix}SO_2\\ (CH_3)_2\end{matrix}\right\}O_2\end{cases}$$

In the same volume, therefore, chloride of acetyl contains the radical chlorine once, while chloride of sulphuryl contains it twice. In the same volume, again, sulphate of methyl contains twice the quantity of methyl that is contained in the acetate. With these differences of composition of the chlorides and neutral ethers are connected other properties, such as the following:—Acetic acid forms but one compound ether, whereas sulphuric acid forms two, a neutral and an acid ether; acetic acid forms but one amide, sulphuric acid forms several, &c. In short, on inquiring what are the smallest quantities of the radicals acetyl and sulphuryl that are concerned in chemical metamorphoses, we find that they are C_2H_3O, equivalent to H; and SO_2, equivalent to H_2; hence we are led to represent the molecule of acetic acid as monatomic, and that of sulphuric acid as biatomic."

605. Many of the organic acids are contained in plants, either in the free state, or under the form of salts. They are produced in very great numbers in treating other organic matters by oxidizing agents, such as nitric acid, chromic acid, peroxide of lead, hydrate of potash, &c. The energetic agents, such as nitric acid, or the mixture of peroxide of manganese and sulphuric acid, produces acids whose composition is much removed from the organic materials employed; oxalic acid and formic acid are obtained frequently in this kind of oxidation. The nitric acid and the sulphuric acid give also sometimes conjugated acids.

Monatomic Acids.

606. The substitution of an acid radical for one atom of hydrogen in one molecule of water gives the acid proper,

or the primary derivative; the substitution of two atoms of the acid radical for the two atoms of hydrogen in one molecule of water gives the acid anhydride, or the secondary derivative.

607. Generally monabasic acids are volatile without decomposition. Their aqueous or alcoholic solutions turn litmus red. When they exchange their basic atom of hydrogen for a metal, a neutral salt is produced.

608. The monobasic acids do not generally give acid salts by double decomposition. In some cases, nevertheless, acid salts are obtained by dissolving a neutral salt in a monobasic acid; acetate of potash, for example, in acetic acid; but these acid salts are decomposed by water.

609. A monobasic acid gives with each alcohol but one ether salt, which is neutral; it does not give an acid ether salt.

610. The ammonia salts of these acids yield by their decomposition but one class of amides—the primary amides; they furnish neither secondary amides (imides), nor acid amides. Sometimes these ammoniacal salts are volatile without decomposition.

(1.) MINERAL ACIDS.

611. The following are the principal monobasic inorganic acids:—

ACIDS PROPER.

Primary derivatives.		Secondary derivatives.	
Nitric acid -	$\left.\begin{matrix}(N O_2)\\ H\end{matrix}\right\} O$	Nitric anhydride -	$\left.\begin{matrix}(N O_2)\\ (N O_2)\end{matrix}\right\} O$
Hypochlorous acid - -	$\left.\begin{matrix}Cl\\ H\end{matrix}\right\} O$	Hypochlorous anhydride -	$\left.\begin{matrix}Cl\\ Cl\end{matrix}\right\} O$
Chloric acid -	$\left.\begin{matrix}(Cl O_2)\\ H\end{matrix}\right\} O$	Chloric anhydride - -	$\left.\begin{matrix}(Cl O_2)\\ (Cl O_2)\end{matrix}\right\} O$
Iodic acid -	$\left.\begin{matrix}(I O_2)\\ H\end{matrix}\right\} O$	Iodic anhydride - -	$\left.\begin{matrix}(I O_2)\\ (I O_2)\end{matrix}\right\} O$
Metaphosphoric acid -	$\left.\begin{matrix}(P O_2)\\ H\end{matrix}\right\} O$	Metaphosphoric anhydride	$\left.\begin{matrix}(P O_2)\\ (P O_2)\end{matrix}\right\} O$

(2.) ORGANIC ACIDS.

612. The monobasic organic acids cannot be transformed into anhydrides by means of double decomposition; neither do dehydrating agents, such as phosphoric anhydride, transform them.

613. Many of the monobasic organic acids give, under the influence of chlorine, of bromine, and of nitric acid,

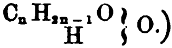
conjugated *monobasic* acids. With sulphuric acid they give likewise conjugated acids, but these are *bibasic*.

614. Treated with perchloride of phosphorus, the monobasic organic acids give the corresponding negative or acid chloride, hydrochloric acid and oxy-chloride of phosphorus being also formed.

615. The proportion of oxygen contained in the monobasic organic acids is generally much less than in the bibasic acids. This is especially the case with the monobasic volatile acids; they contain, in their molecule, two or three atoms of oxygen; whilst the bibasic acids contain not less than four atoms.

FIRST CLASS.

(*The general formula of this class is,*



$\left.\begin{matrix}C_nH_{2n-1}O\\H\end{matrix}\right\}O$.)

616. The first class of alcohols and their aldehydes yield by oxidation this class of acids, as we have already shown (par. 563), by a general equation. Many of them occur in the vegetable and animal organisms, in combination with glycerine, forming oils or fats, from which substances they are separated by the process of saponification. Some of them are formed by the action of oxidizing agents on fatty and waxy matters, and some of them are also formed by the action of the same agents on albumen, fibrine, caseine, &c.

617. The members of this group, like the members of all other groups of homologous bodies, possess analogous properties. All the members of this group can be distilled without undergoing decomposition. With the exception of the first two (formic and acetic acids), they all possess the characters of an oil. They are, with the exception of the first two, imperfectly soluble in water, although some of the lower members of the series dissolve to a considerable extent in water; they all dissolve readily in alcohol and ether. The first ten acids in the group are liquid at ordinary temperatures; the next four are solid fats; the last two are waxy substances.

618. Although these acids constitute one of the most numerous, and also the most carefully examined groups of homologous compounds, still, if melissic acid is the extreme limit, which there is no reason for supposing, we

can see that all the members of the group have not yet been discovered. Several members have yet to be discovered to fill up the gap between stearic acid and cerotic acid, and again between this last acid and melissic acid several members are still wanting. Sixteen acids belonging to this class have already been discovered.

619. These acids are called the fatty acids, on account of the greater number of them being oily bodies,* and being constituents of the oils and fats.

620. The student must now commit to memory the names and symbols of these acids.

Names.	Formulæ.	Melting point, 0° F.	Boiling point, 0° F.	Whence obtained.	
Formic acid	$\left.\begin{matrix}(C\,H\,O)\\H\end{matrix}\right\}O$	21	221	Red ants; distillation of oxalic acid; and oxidation of amylaceous and other organic bodies.	
Acetic	$\left.\begin{matrix}(C_2H_3O)\\H\end{matrix}\right\}O$	63	243	Distillation of wood; oxidation of alcohol, &c.	By oxidation of oleic acid with nitric acid.
Propionic	$\left.\begin{matrix}(C_3H_5O)\\H\end{matrix}\right\}O$	...	284	Fermentation of glycerine, &c.	
Butyric	$\left.\begin{matrix}(C_4H_7O)\\H\end{matrix}\right\}O$	below 0	314	Butter; fermentation of lactic acid.	
Valerianic	$\left.\begin{matrix}(C_5H_9O)\\H\end{matrix}\right\}O$	below 0	347	Valerian root; oxidation of amylic alcohol.	
Caproic	$\left.\begin{matrix}(C_6H_{11}O)\\H\end{matrix}\right\}O$	...	392	Butter	
Œnanthylic	$\left.\begin{matrix}(C_7H_{13}O)\\H\end{matrix}\right\}O$	below 0	298 (?)	Castor oil, by distillation, &c.	
Caprylic	$\left.\begin{matrix}(C_8H_{15}O)\\H\end{matrix}\right\}O$	59	457	Butter, cocoa-nut oil.	
Pelargonic	$\left.\begin{matrix}(C_9H_{17}O)\\H\end{matrix}\right\}O$	...	500	Leaves of the geranium.	
Rutic (capric)	$\left.\begin{matrix}(C_{10}H_{19}O)\\H\end{matrix}\right\}O$	86	...	Butter; oil of rue, by oxidation.	
Lauric	$\left.\begin{matrix}(C_{12}H_{23}O)\\H\end{matrix}\right\}O$	110	...	Cocoa-nut oil; berries of the bay-tree.	
Myristic	$\left.\begin{matrix}(C_{14}H_{27}O)\\H\end{matrix}\right\}O$	129	...	Nutmeg butter, cocoa-nut oil, &c.	
Palmitic	$\left.\begin{matrix}(C_{16}H_{31}O)\\H\end{matrix}\right\}O$	143·8	...	Palm oil, butter, bees-wax, &c.	
Stearic	$\left.\begin{matrix}(C_{18}H_{35}O)\\H\end{matrix}\right\}O$	159	...	Most solid animal fats.	
Cerotic	$\left.\begin{matrix}(C_{27}H_{53}O)\\H\end{matrix}\right\}O$	174	...	Beeswax.	
Melissic	$\left.\begin{matrix}(C_{30}H_{59}O)\\H\end{matrix}\right\}O$	192	...	Beeswax.	

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* All the oily acids are not, however, comprised in this group. Oleic acid, for example, is a member of the next group.

621. The student, on examining the table, will see that each member, as far as rutic acid, differs from the one below it by an increase of CH_2; but from rutic up to stearic, they increase by C_2H_4. It is generally supposed by chemists that C_2H_4 is the true rate of increase in the higher terms of the series, and these do not, like the lower terms, increase by CH_2; but if the formula of cerotic acid be correct, the rate of increase up through the whole series must be by CH_2. Heintz has suggested, that cerotic acid may be a mixture of two other acids, since he finds it to be a general rule that a mixture of any two of the solid acids of this series has a fusing point considerably below that of either of its components; and the fusing point of cerotic acid is lower than one would expect for an acid so high in the series.

622. The mean rise of the boiling-point in the acids for each additional equivalent of CH_2, is 38·9° F. Their fusing or melting points likewise increase with the increase in the quantity of carbon and hydrogen.

623. These monobasic acids form both neutral and acid salts* with the alkalies. Many of them yield, with oxide of lead, not only the neutral salt, but also basic salts, which contain three equivalents of oxide of lead for each equivalent of acid.

624. If the student will compare the table of the first class of alcohols with this table of acids, he will see that for every alcohol there is a corresponding acid; and he will also see that the alcohols of several of these acids are still undiscovered. We can convert the alcohols into their corresponding acids, but we cannot yet convert the acids into their corresponding alcohols.† That is, we cannot yet remove the oxygen in the acid, and replace it by hydrogen, so as to form the alcohol of the acid, although we can replace the hydrogen in the alcohols by oxygen.

625. We have already considered (par. 466) the substances into which these acids are decomposed, when their alkaline salts are submitted to the action of a galvanic current. Kolbe, who studied these decompositions, consi-

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* We have already noticed the acid acetates (608).

† As we can now convert aldehydes and acetones into alcohols, we may, by converting the acids into one or other of these bodies, obtain the missing alcohols.

dered at one time that the decomposition-products proved that these acids are conjugate compounds of oxalic acid and the alcohol radical which is separated during the electrolysis of the acid. Acetic acid, for instance, is, on this view, oxalic acid coupled with methyl [$HO,(C_2H_3)C_2O_3$*]. Gerhardt and Wurtz regard all the other acids of the series as derivatives of formic acid, by containing, in place of the non-basic atom of hydrogen in formic acid, an atom of one of the alcohol radicals, as ethyl, butyl, &c.

626. We must here notice some new and very interesting methods for the formation of these acids. Kolbe and Schmitt have prepared formic acid direct from inorganic substances, for they have transformed carbonic acid direct into formic acid, which they did in the following way:—They placed some thin shavings of potassium in a capsule; they placed the capsule under a bell glass, which was filled with carbonic acid, and they prevented the access of air into the bell glass by letting it rest in a bell of lukewarm water. In about twenty-four hours, a mixture of bicarbonate of potash and formiate of potash was formed. The reaction is produced according to the following equation:—

$$2K + 2CO_2 + H_2O = \left.\begin{matrix} CHO \\ K \end{matrix}\right\} O + \left.\begin{matrix} (CO)'' \\ HK \end{matrix}\right\} O_2$$

627. They isolated the formic acid by treating the mixed salts with sulphuric acid, and distilling; neutralizing the acid liquor in the receiver with carbonate of lead; the solution of the lead thus obtained gave pure formiate of lead.

628. Sodium furnished, under the same circumstances, a less quantity of formic acid than the potassium.

629. Wanklyn has prepared acetic acid and propionic acid by the action of dry carbonic acid on sodium methyl and sodium ethyl:—

$$(1.)\ NaCH_3 + CO_2 = \left.\begin{matrix} C_2H_3O \\ Na \end{matrix}\right\} O$$

$$(2.)\ NaC_2H_5 + CO_2 = \left.\begin{matrix} C_3H_5O \\ Na \end{matrix}\right\} O$$

630. The sodium compounds he formed by adding sodium to zinc methyl, and to zinc ethyl. A part of the

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* The old atomic weights are used in this formula ($O = 8$, $C = 6$).

zinc was precipitated, and he got a double compound of the sodium and zinc compound; and on this double compound he operated with the carbonic acid, which acts only on the sodium body, the zinc compound separating.

631. When the cyanides of the alcohol radicals of the first class are heated with the caustic alkalies, acids belonging to this group are formed:—

$$(C_nH_{2n+1}),CN + \left.\begin{matrix}K\\H\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}O = \left.\begin{matrix}C_nH_{2n-1}O\\K\end{matrix}\right\}O + NH_3$$

632. *Substitution of other radicals for the hydrogen in the radicals of the acids.*—The hydrogen in the acid radicals can be replaced by chlorine, bromine, or iodine. We can produce, for instance,—

Monochloracetic acid.	Bichloracetic acid.	Trichloracetic acid.
$\left.\begin{matrix}(C_2H_2ClO)\\H\end{matrix}\right\}O$	$\left.\begin{matrix}(C_2HCl_2O)\\H\end{matrix}\right\}O$	$\left.\begin{matrix}(C_2Cl_3O)\\H\end{matrix}\right\}O$

633. The chloroconjugated acids are most frequently produced by the direct action of chlorine, or of hypochlorous acid, upon the acids. The bromo and iodo acids are produced by the action of bromine, or bromide of iodine, or chloride of iodine, upon the acids.

634. The basicity of these conjugated acids is the same as that of the normal acids. The chlorine, &c., is not removed by a salt of silver; the presence of the substituted element cannot be discovered without destroying the compound. The conjugated acids resemble the normal ones in their characters.

635. Chlorine, &c., can not only be substituted for the hydrogen of the normal acids, but we can also substitute hydrogen for the chlorine, &c., of the conjugated acids, and so reproduce the normal acids; this fact proves that the substitution of one element for another in a chemical molecule does not change the constitution of the molecule. The regeneration of the normal acids from the conjugated ones was effected, for the first time, by M. Melsens, upon trichloracetic acid, by means of an amalgam containing about 150 parts of mercury for every one part of potassium.* He poured an aqueous solution of the

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* The amalgam is employed instead of pure potassium, in order to moderate the action; it has also this advantage over the pure metal, it divides the potassium more completely.

conjugated acid, or the potash salt of the acid, upon the amalgam; at the moment of the mixture the temperature is considerably elevated; if the solution is very concentrated, a saline solid is formed in great abundance. Whether the liquid was neutral or acid to commence with, it becomes, during the transformation, strongly alkaline; and if a slight excess of the conjugated compound in proportion to the potassium is employed, there is not a trace of gas disengaged during the whole of the reaction, and the change is effected in a very short time. The saline mass is composed of acetate of potash, mixed with chloride of potassium and caustic potash.

636. The reaction which takes place may be thus expressed:—

(1.) $3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + 3\,K\,K = 3\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) + 3\,H\,K$

(2.) $\left.\begin{matrix}(C_2\,Cl_3\,O)\\K\end{matrix}\right\}O + 3\,H\,K = \left.\begin{matrix}(C_2\,H_3\,O)\\K\end{matrix}\right\}O + 3\,K\,Cl$[*]

637. If we distil the alkaline salts of these acids with an excess of potash, we obtain a member of the marsh gas series, and carbonate of potash is left in the retort. Example:—

$$\left.\begin{matrix}(C_2\,H_3\,O)\\K\end{matrix}\right\}O + \left.\begin{matrix}K\\H\end{matrix}\right\}O = C\,H_4 + \left.\begin{matrix}(C\,O)''\\K_2\end{matrix}\right\}O_2$$

638. If we distil trichloracetate of potash with an excess of potash, we get chloroform and carbonate of potash, thus:—

$$\left(\begin{matrix}C_2\,Cl_3\,O\\K\end{matrix}\right)O + \left.\begin{matrix}K\\H\end{matrix}\right\}O = C\,H\,Cl_3 + \left.\begin{matrix}(C\,O)''\\K_2\end{matrix}\right\}O_2$$

639. Chloroform and marsh gas (hydride of methyl) are corresponding chemical bodies; we can convert the marsh gas into chloroform by the action of chlorine; this is another proof that the substitution of one element for

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[*] The chlorine may either be removed at once, or we may suppose that the trichloracetate passes into bichloracetate, this into monochloracetate, and this last into normal acetic acid.

Zinc can, at least in some cases, remove chlorine and substitute hydrogen, thus regenerating from the conjugate compound the normal acid.

Sometimes the exchange of the second atom, and especially of the third atom of chlorine is effected with more difficulty than the exchange of the first atom. This proves, I think, that the bichlor-compounds do not pass at once into the normal acid, but gradually, by the successive replacement of each chlorine atom.

another in a chemical molecule does not change the constitution of the molecule.

640. In some of the higher members of the series an atom of hydrogen in the radical can be replaced by NO_2; this substitution will be noticed at further length in the third series of acids.

641. In several of these acids one or two atoms of hydrogen in the radical can be replaced by SO_2; this substitution will be noticed at further length in the third series of acids.

642. *The acid anhydrides.*—The anhydrides of the organic monobasic acids are produced by the reaction of the chlorides of the acid radicals upon the alkaline salts of the corresponding acids:—

$$\left.\begin{matrix}(C_2H_3O)\\ K\end{matrix}\right\}O + Cl,\ C_2H_3O = \left.\begin{matrix}(C_2H_3O)\\ C_2H_3O\end{matrix}\right\}O + KCl$$

Two different radicals can replace the two atoms of hydrogen in the molecule of water; we then get mixed anhydrides. Example:—

Anhydride aceta-benzoique.

$$\left.\begin{matrix}(C_2H_3O)\\ K\end{matrix}\right\}O + Cl,\ C_7H_5O = \left.\begin{matrix}C_2H_3O\\ C_7H_5O\end{matrix}\right\}O + KCl$$

643. We can also obtain the anhydrides by acting upon the alkaline salts of the corresponding acids with oxychloride of phosphorus; there are, as it will be seen, two different stages in the reaction; there is, first, the formation of the chloride of the acid radical, and then the formation, by the action of this chloride, of the acid anhydride:—

$$(1.)\ 3\left(\left.\begin{matrix}C_2H_3O\\ K\end{matrix}\right\}O\right)+Cl_3,PO=3(Cl,\ C_2H_3O) + \left.\begin{matrix}(PO)'''\\ K_3\end{matrix}\right\}O_3$$

$$(2.)\ 3\left(\left.\begin{matrix}C_2H_3O\\ K\end{matrix}\right\}O\right)+3\,(Cl,C_2H_3O)=3\left(\left.\begin{matrix}C_2H_3O\\ C_2H_3O\end{matrix}\right\}O\right)+3KCl$$

644. The anhydrides of the monobasic organic acids are liquid or solid; when they contain only one radical they are generally volatile without decomposition. The anhydrides containing two different radicals (the mixed anhydrides) are decomposed by heat into two anhydrides, each containing but one radical:—

$$2\left(\left.\begin{matrix}C_2H_3O\\C_7H_5O\end{matrix}\right\}O\right)=\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O+\left.\begin{matrix}C_7H_5O\\C_7H_5O\end{matrix}\right\}O$$

645. The anhydrides of the monobasic organic acids are little soluble in water; they are converted more or less rapidly, under the influence of this liquid, into the hydrated acids (acids proper); the presence of an alkali determines promptly this transformation.

646. Ether dissolves these anhydrides without alteration; alcohol also dissolves them, but a very little of the ether salt of the acid is formed.

647. In contact with ammonia, the anhydrides of the monobasic organic acids give neutral amides.

648. *Substitution of oxygen in the acids proper and the anhydrides by sulphur, &c.*—Sulphur can be exchanged for the oxygen in the acids, by acting upon them with persulphide of phosphorus. Example:—

$$5\left(\left.\begin{matrix}(C_2H_3O)\\H\end{matrix}\right\}O\right)+P_2S_5=5\left(\overset{\text{Thionacetic acid.}}{\left.\begin{matrix}(C_2H_3O)\\H\end{matrix}\right\}S}\right)+P_2O_5$$

These acid sulphides form salts with the bases like the oxygen acids.

649. The anhydrides of the sulphur acids can be obtained by the two following methods:—1. By acting upon the chlorides of the acid radicals with the sulphur bases; 2. By acting upon the oxygen anhydrides with persulphide of phosphorus. Examples:—

$$(1.)\ 2\,(Cl,C_2H_3O)+\left.\begin{matrix}Pb\\Pb\end{matrix}\right\}S=2\,Pb\,Cl+\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}S$$

$$(2.)\ 5\left(\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O\right)+P_2S_5=5\left(\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}S\right)+P_2O_5$$

650. As these acids are met with constantly, both in animal and vegetable products, and as they seldom occur singly, we will describe the methods usually employed for their separation. When the presence of these acids is indicated, we have first of all to ascertain whether more than one acid is present. One of two physical tests, the boiling point or melting point, is usually employed to ascertain this. If the acid substance is liquid at the common temperature, we determine the boiling point; if this does not agree with the boiling point of any of the known acids, or does not differ from the boiling point which is

nearest by about 38·9° F., or some multiple of that number, we may almost conclude with certainty that more than one acid is present. We must then adopt either Heintz's method (652), or Liebig's method (655), for their separation.

651. If the acid substance is *solid* at the common temperature, we determine its melting point; we then crystallize it from hot alcohol or ether, and again determine the melting point of that portion which has been deposited from the alcohol; if the melting points of the purified and unpurified portion are the same, we infer that only one acid is present, but in order to be perfectly certain, it is better also to examine the substance according to Heintz's method (652); but if the melting points are not the same, we continue to recrystallize the substance from alcohol until we get a constant melting point. When this is accomplished, we may analyse this portion in the usual way.

652. The method of Heintz is based upon the following fact, that when a mixture of substances is treated with a substance for which they all have affinity, but not in sufficient quantity to saturate the whole, those whose affinity is greatest will of course enter into combination with the substance. Heintz dissolves the fatty acids in so much boiling alcohol that no separation takes place on cooling; to the boiling solution an *alcoholic* solution of acetate of lead is added in small quantities at a time, in the proportion of a third part by weight of the acid mixture. Should a precipitate form in the boiling solution, some acetic acid is added until the solution has again become clear; it is then allowed to cool, the precipitate which forms brought upon a filter and pressed. The liquid filtered from the precipitate is mixed with a small excess of an alcoholic solution of acetate of lead, filtered, and the precipitate likewise submitted to pressure.

653. The lead salts obtained in this manner are decomposed, either by boiling them in very dilute hydrochloric acid, or, as this decomposition proceeds very slowly, on account of the sparing solubility of chloride of lead, by boiling them in hot alcohol, to which some hydrochloric acid is added; the alcoholic solution of the fatty acids thus obtained must subsequently be boiled with caustic potash, on account of the possible formation of the ether of the fatty acids, and after the alcohol has been expelled by

evaporation, the potash soap must be decomposed by hydrochloric acid.

654. If the two portions thus obtained have not the same melting point, each of these portions (which we shall call A and B, in order to render the description more intelligible) is again separated, by the fractional precipitation with acetate of lead, into *two* portions; and if the two portions, into which the A portion, and the two portions, into which the B portion, have been divided, have not the same melting point, each of these portions must be separated by the fractional precipitation into two; *the operation is repeated until the two portions, into which a previous portion has been divided, have the same melting point.* After each fractional precipitation, the acid ought to be re-crystallized from alcohol, before determining the melting point.*

655. Liebig's method consists in partially saturating the acid solution with potash, and then separating by distillation the unneutralized from the neutralized portion. It is thus performed:—The mixture—say of butyric and valerianic acids—is divided into two portions, one of which is neutralized with potash or soda; the other portion of the acid is then added to the neutralized portion, and the whole subjected to distillation. One of two cases will now occur,—if the valerianic acid in the mixture amounts to more than is sufficient to neutralize the whole of the alkali, the residue contains no butyric acid, but pure valerianic acid. If the quantity of the valerianic acid be less, a proportionate amount of butyric acid is left with the whole of the valerianic acid in the residue; but the distillate consists of pure butyric acid.

656. The quantity of the mixed acids which is neutralized with alkali, must be measured by the amount of the valerianic acid supposed to exist in the mixture. For instance, assuming ten per cent. of valerianic acid, then one-tenth of the mixture is neutralized; but supposing it to be a valerianic acid containing ten per cent. of butyric acid, which it is wished to separate, then nine-tenths of the acid must be neutralized.

657. It is readily perceived that by a single operation one of the acids is always obtained pure. Either the

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* The student will find Heintz's paper on the separation of the fatty acids in the *Chemical Gazette*, vol. ix.

distillate is pure butyric acid, and then the residue consists of a mixture of valerianic and butyric acids, or the distillate contains butyric and valerianic acids at the same time, and in this case the residue contains pure valerianic acid. By continuing the same treatment of the mixed residue or of the mixed distillate, *i. e.*, partial saturation and distillation, it is possible to obtain from the residue another portion of one or other of the acids pure; and, finally, a perfect separation is effected, such as is scarcely possible by mere distillation of the acids.

658. As the boiling points of these two acids differ, it will be imagined that the soda, on combining with the least volatile of the acids, the valerianic, deprives it, by neutralizing it, of its volatility at the temperature at which the other acid in the mixture boils, and consequently the butyric acid can be distilled off in a pure state, whilst the neutralized valerianic acid remains behind in the retort.

659. A mixture of valerianic with acetic acid, or of butyric with acetic acid, behaves in a totally different manner under the same circumstances. When such a mixture is partially neutralized with potash, and then submitted to distillation, it would be expected that acetic acid, on account of its lower boiling point, would principally pass over. Such, however, is not the case; but the two other acids distil over, although the boiling point of acetic acid is more than 90° F. lower than that of butyric acid, and more than 126° lower than that of valerianic acid. This is owing to the formation of an acid acetate, which does not appear to be decomposed by either of the other two acids.

660. If valerianic acid is added to a solution of neutral acetate of potash, it instantly dissolves, and in large quantity. In binacetate of potash, the valerianic acid floats in oily drops upon the surface, and appears not to dissolve therein to a greater extent than in water. If a solution of neutral acetate of potash, to which an excess of valerianic acid has been added, is submitted to distillation, valerianic acid passes over, and the residue contains binacetate of potash, together with valerianate of potash. If valerianic acid is added to binacetate of potash, and the mixture distilled, valerianic acid passes over, and the binacetate is left in the retort free from valerianic acid. Butyric acid behaves precisely like valerianic acid. While,

therefore, butyric or valerianic acid, containing acetic acid, is partially saturated with potash, and distilled, either the whole of the acetic acid is left as an acid salt, together with butyric acid, and in this case the acid which passes over is pure, and free from acetic acid, or only acetic acid is left in the residue; and in this case the distillate still contains acetic acid, which can be separated from the butyric or valerianic acid by a similar operation.[*]

661. *Determination of the melting point of fusible organic bodies.*—We shall here describe the method for determining the melting or freezing of organic substances, when only a small quantity of the substance is available for experiment. The temperature at which a body melts coincides in general with the temperature at which it becomes solid after it has been melted; it is therefore advantageous, in determining the melting point of any body, to determine also the temperature at which it solidifies. If the temperature at which the body melts and that at which it solidifies do not coincide, the melting point should be taken as the physical constant, rather than the freezing point, for the reasons explained in the foot-note.[†]

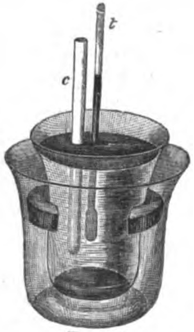

FIG. 19.

662. The apparatus represented in Fig. 19 will be frequently found very convenient for determining the

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[*] "On the Separation of some Acids of the Series $\left.\begin{matrix}C_nH_{2n-1}O\\H\end{matrix}\right\}O$." By Baron Liebig. Liebig's *Annalen*, Sept., 1849, or 8th vol. *Chemical Gazette*.

[†] "If a substance in the liquid form is cooled below the temperature at which it melts, it again becomes solid; and, as a general rule, the freezing point is the same as the freezing point. But in many cases we can cool a liquid several degrees below its melting point, without its solidifying. Thus by keeping water perfectly still, we can succeed in cooling it to 5° F., or even to 1·4° F., before it freezes. If, however, when in this condition, we drop into the water an angular body, like a piece of sand, or gently jolt the vessel containing it, congelation begins at once, and the temperature suddenly rises to 32°. This singular phenomenon seems to be caused by the inertia of the particles of the liquid, and is exhibited to a still greater degree in viscid liquids, like the fats, where, on account of the imperfect fluidity, the inertia is greater. Such liquids uniformly do not *begin* to freeze until they are cooled several degrees below the melting point; but as soon as the change commences, the temperature at once rises to this point. It has been noticed that the phenomenon just described is most readily produced when the liquid is enclosed in a capillary tube."—*Cook's* "*Chemical Physics*."

melting or freezing point of many organic substances, especially when only a small quantity is available for the experiment. It consists of a water or oil bath, made with two beaker glasses (one supported within the other, as represented in the figure), so that the conduction of heat from the lamp to the inner vessel may be as uniform as possible. A thermometer (*t*) in the inner glass gives the temperature of the bath at each instant; and the substance under experiment, enclosed in a thin capillary glass tube (*c*), is immersed in the bath at the side of the thermometer. By slowly heating (by means of a spirit or other lamp) and then allowing the bath to cool slowly, it is easy to catch the exact point at which the solid melts, and the liquid again freezes; and the experiment can readily be repeated a great number of times.

SECOND CLASS.

(*The general formula of this class is,* $\left.\begin{matrix} C_n H_{2n-3} O \\ H \end{matrix}\right\} O.$)

663. With the exception of one alcohol and one aldehyde, the alcohols and aldehydes of this class of acids are yet undiscovered. Allylic alcohol and acrolein, the known alcohol and aldehyde, are the alcohol and aldehyde of acrylic acid.

664. The acids of this class correspond in their physical properties with the acids comprising the first class. There is the same decrease in their volatility and solubility as the bodies increase in atomic weight. The higher members of this class cannot be distilled without undergoing decomposition.

665. These acids possess the remarkable property of being converted by peroxide of nitrogen into metameric acids, which require a much higher temperature for their fusion than the oily acids from which they are obtained; the metameric acids may be distilled unchanged. These acids also absorb oxygen with great facility. From the difficulty of purifying them, on account of their indisposition to crystallize, from the substances produced by this oxidation, the investigation of these acids is attended with considerable difficulty. This class of acids has therefore been less perfectly studied than the former class.

666. Oleic acid, on account of its being the principal acid in most oils, and generally a constituent, in a greater

or less degree, of fats as well as oils,—is, on account of this wide distribution, and the properties of its glycerine compound (olein), the most important member of the class.

667. The following table contains the names of the acids of both isomeric series which are at present known. The formulæ of some of the terms will probably be modified hereafter:—

LIQUID ACIDS.

		Fusing point.	Origin.
Acrylic - -	$\left.\begin{matrix}C_3H_3O\\H\end{matrix}\right\}O$	...	Distillation of glycerine
Moringic - -	$\left.\begin{matrix}C_{15}H_{27}O\\H\end{matrix}\right\}O$	32° F.	Oil of ben
Physetoleic -	$\left.\begin{matrix}C_{16}H_{29}O\\H\end{matrix}\right\}O$	...	Sperm whale
Oleic - -	$\left.\begin{matrix}C_{18}H_{33}O\\H\end{matrix}\right\}O$	57°	Non-drying oils
Doeglic - -	$\left.\begin{matrix}C_{19}H_{35}O\\H\end{matrix}\right\}O$	62°	The Dōgling whale
Erucic - -	$\left.\begin{matrix}C_{22}H_{41}O\\H\end{matrix}\right\}O$	93°	Mustard seed and rapeseed

METAMERIC SOLID ACIDS.

		Fusing point.	Origin.
Angelic - -	$\left.\begin{matrix}C_5H_7O\\H\end{matrix}\right\}O$	113° F.	Angelica root; it is also produced by the action of potash upon essence of camomile
Elaidic - -	$\left.\begin{matrix}C_{18}H_{33}O\\H\end{matrix}\right\}O$	113°	Action of NO_4 on oleic acid

668. The acids of this class all possess the characteristic reaction of breaking up into acetic acid and a second acid of the acetic series, when gently heated with hydrate of potash, hydrogen being at the same time evolved, as is shown by the following general equation:—

$$\left.\begin{matrix}C_nH_{2n-3}O\\H\end{matrix}\right\}O + 2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) = \left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O$$
$$+ \left.\begin{matrix}C_nH_{2n-1}O\\K\end{matrix}\right\}O + 2\,H$$

669. The metameric acids also break up into acetic acid and a second acid of the acetic series, when heated with

hydrate of potash, hydrogen being at the same time evolved.

670. This class of acids has been so little studied, that few or in some cases no experiments have been made as regards the substitution of the hydrogen in the acids by other radicals, or by the substitution of sulphur or other bodies for the oxygen, nor have their alkaline salts been submitted to the action of a galvanic current.

671. Before concluding our observations upon this class of acids, we must make some further remarks upon oleic acid and its compounds, and upon the metameric acids.

672. "Oleic acid forms two classes of salts, neutral and acid. The neutral salts of the alkalies are the only soluble ones. They form soaps, and by the evaporation of their aqueous solution they may be obtained in the condition of an amorphous mass. Oleate of potash forms a soft soap, which is the chief ingredient in Naples soap. Oleate of soda is a hard soap, and enters largely into the composition of Marseilles soap. The acid oleates of the alkalies are liquid and insoluble. The metallic oleates, such as those of copper and lead, are soluble in cold anhydrous alcohol and in ether; they are thus separable from the stearates and palmitates, which are insoluble in these liquids."—*Miller*.

673. Oleic acid cannot be distilled without undergoing decomposition; a large quantity of liquid and gaseous hydrocarbons is given off, besides acetic, caprylic, and capric acids, and probably other acids of the acetic series; but the most characteristic product is the bibasic acid, sebacic acid, the presence of which in the products obtained by distilling any oil is a sure test of the presence of oleine in that oil.

674. "When oleic acid is subjected, in a capacious retort, to the action of a large excess of nitric acid, of sp. gr. 1·42, diluted with an equal bulk of water, it gradually disappears, producing a copious evolution of nitrous fumes, attended with a violent reaction. The results of the decomposition are very complicated, but the products obtained by this method of oxidizing oleic acid present considerable interest, since they contain, according to Redtenbacher, all the terms of the homologous series of the fatty acids, from the acetic to the capric acid inclusive, these acids being found in the distillate; whilst, according to Laurent, four fixed acids are left in the retort, and

these form contiguous terms of a group of homologous dibasic acids of the general formula, $\left.\begin{matrix}(C_nH_{2n-4}O_2)''\\H_2\end{matrix}\right\}O_2$. The quantity of the volatile acids is greater when the nitric acid used is very concentrated; if it be more dilute, that of the fixed acids is increased. The fixed acids which remain in the retort are the following:—

Suberic acid - - - -	$\left.\begin{matrix}(C_8H_{12}O_2)''\\H_2\end{matrix}\right\}O_2$
Pimelic acid - - - -	$\left.\begin{matrix}(C_7H_{10}O_2)''\\H_2\end{matrix}\right\}O_2$
Adipic acid - - - -	$\left.\begin{matrix}(C_6H_8O_2)''\\H_2\end{matrix}\right\}O_2$
Lipic acid - - - -	$\left.\begin{matrix}(C_5H_6O_2)''\\H_2\end{matrix}\right\}O_2$

It is interesting to remark that another acid of this group, viz., the sebacic acid, $\left.\begin{matrix}(C_{10}H_{16}O_2)''\\H_2\end{matrix}\right\}O_2$, is a characteristic product of the distillation of oleic acid; and succinic acid, $\left.\begin{matrix}(C_4H_4O_2)''\\H_2\end{matrix}\right\}O_2$, which is one of the most frequent products of the action of nitric acid upon the series of fatty acids, is the next term below the lipic acid."* These dibasic acids will be described in their proper place.

675. Oleic acid and oleine, or oils containing oleine, are rapidly solidified by contact with nitrous acid, or with a solution of nitrate of mercury, which yields nitrous acid, the solidification being due to the conversion of oleic acid into the solid metameric acid—elaidic acid. The cause of this remarkable change is unknown; the oleic acid yields an equal weight of elaidic acid; the nitrous acid appears to undergo no change, and only a very small quantity is required, not exceeding $\frac{1}{200}$ of the weight of the oleic acid.

676. Although no liquid acid of the composition of angelic acid has yet been discovered, and therefore it has not yet been ascertained whether angelic acid could be prepared like elaidic acid, by acting upon a liquid acid of the same composition as itself by means of nitrous acid, yet, from its high fusing point, and from its distilling without decomposition, it is considered to belong to the elaidic group.

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* Miller's "Elements of Chemistry," vol. iii.

THIRD CLASS.

(*General formula,* $\left.\begin{matrix}C_nH_{2n-5}O\\H\end{matrix}\right\}O.$)

677. In the juice of the unripe berry of the mountain ash there exists a volatile acid, along with malic acid. This acid Hofmann has recently examined. It constitutes a transparent, oily, colourless liquid, of a peculiar aromatic odour, not unpleasant when dilute, but rather disagreeable and almost overpowering when concentrated. An analysis of its silver salt led to the following formula for the acid:—

$$\left.\begin{matrix}C_6H_7O\\H\end{matrix}\right\}O$$

When this oily acid is gently heated with *solid* hydrate of potash, an unexpected transformation takes place. The product of the reaction, dissolved in water, and saturated with hydrochloric acid, furnishes an oil which rapidly solidifies into a hard crystalline compound, possessing the characters of a well defined acid. This observation at once suggested to Hofmann the idea of aldehyde and acid, but it was found that the transformation takes place without the evolution of a trace of hydrogen. Several grammes of the oil were heated for two or three hours in a sealed tube with hydrate of potash, in a water bath. Not a trace of gas was disengaged when, after cooling, the tube was opened under water, but the oil was almost entirely converted into the crystalline acid. The same molecular transformation, as might have been expected, is produced by the action of acids. On boiling the oil for a short time with concentrated hydrochloric acid, it becomes more and more viscid, and ultimately solidifies. A similar result is produced by sulphuric acid. The oily acid dissolves in concentrated sulphuric acid; the oil, which re-precipitates on addition of water, gradually becomes a solid crystalline mass.

678. The mode of forming the new acid suggested the probability of its being isomeric with the original oil. This suggestion has been fully borne out by experiment. Hofmann has designated the solid acid sorbic, a name once used for malic acid, and the oily acid parasorbic acid.

679. The formula of the acid is the same as that of the oily acid, viz.:—

$$\left.\begin{matrix}C_6H_7O\\H\end{matrix}\right\}O$$

680. Sorbic acid is obviously the first term of a new series of well characterised organic acids, closely allied with the ordinary fatty and aromatic acids, occupying, in fact, a sort of intermediate position between the two. On comparing sorbic acid with the terms of the fatty and aromatic acid series, containing an equal number of carbon equivalents, the hydrogen of sorbic acid stands in the middle.

Caproic acid.	Sorbic acid.	Lower homologue of benzoic acid.
$\left.\begin{matrix}C_6H_{11}O\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_6H_7O\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_6H_3O\\H\end{matrix}\right\}O$

681. The same remark applies to the carbon, if sorbic acid be contrasted with the fatty and aromatic acids, containing an equal number of hydrogen equivalents:—

Butyric acid.	Sorbic acid.	Toluic acid.*
$\left.\begin{matrix}C_4H_7O\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_6H_7O\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_8H_7O\\H\end{matrix}\right\}O$

FOURTH CLASS.

(*The general formula of this class is* $\left.\begin{matrix}C_nH_{2n-9}O\\H\end{matrix}\right\}O.$)

682. The physical characters of the acids of this class are different to those of the first two classes; they are solid and crystalline at the ordinary temperature, they are sublimed by heat, and are only slightly soluble in cold water; they are called the aromatic acids. At present we only know three acids of this group; they are the following:—

Benzoic acid - - - - -	$\left.\begin{matrix}C_7H_5O\\H\end{matrix}\right\}O$
Toluic acid - - - - - -	$\left.\begin{matrix}C_8H_7O\\H\end{matrix}\right\}O$
Cuminic acid - - - - -	$\left.\begin{matrix}C_{10}H_{11}O\\H\end{matrix}\right\}O$

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* Dr. A. W. Hofmann, "On New Volatile Organic Acids of the Mountain Ash Berry," vol. xii., *Quarterly Journal of the Chemical Society.*

683. These acids are produced by the oxidation of their alcohols (alcohols of the third class), also by the oxidation of their aldehydes (aldehydes of the third class), and sometimes by the oxidation of the hydrides of their alcohol radicals. Benzoic acid exists in gum benzoin; it also occurs in the urine of herbivorous animals, under certain circumstances.

684. *Substitution of the hydrogen in the acids by other radicals.*—Monochlor, bichlor, and trichlor benzoic acids have been obtained, and similar compounds could also be obtained with the other two acids. Monobrominated benzoic acid has likewise been formed.

685. We have seen that some of the hydrogen in the radicals of the alcohols corresponding to this class of acids can be replaced by $N O_2$ and $S O_2$; some of the hydrogen in these acids can also be replaced by the same radicals. If we boil these acids with an excess of nitric acid, the acid dissolves with a red colour, and binoxide of nitrogen is disengaged. If the boiling is continued for some hours, the formation of the gas keeps constantly decreasing, and at last ceases, and the coloration of the liquid disappears; the solution deposits, when cold, crystals of the acid, in which one atom of hydrogen has been replaced by $N O_2$; the general formula of these acids is, therefore, $\left.\begin{matrix} C_n N O_2, H_{2n-10} O \\ H \end{matrix}\right\} O$. The basicity of the acid is not altered by this replacement; it is still monobasic.*

686. When an alcoholic solution of these nitroacids is saturated with ammonia and sulphuretted hydrogen, this latter body decomposes, and is decomposed by the $N O_2$ in the acid; sulphur is deposited, water formed, and $N O_2$ becomes converted into $N H_2$. The following changes, for instance, take place when nitrobenzoic acid is acted upon by sulphuretted hydrogen:—

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* Several acids of the first class (fatty acid series) also furnish nitro-acids when treated with fuming nitric acid; such, for example, as the following:—

Nitropropionic acid	$\left.\begin{matrix} C_3 H_4 (N O_2) O \\ H \end{matrix}\right\} O$
Nitrobutyric acid	$\left.\begin{matrix} C_4 H_6 (N O_2) O \\ H \end{matrix}\right\} O$
Nitrovaleric acid	$\left.\begin{matrix} C_5 H_8 (N O_2) O \\ H \end{matrix}\right\} O$

$$\left.\begin{matrix}C_7H_4(NO_2)O\\H\end{matrix}\right\}O+3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right)=\overset{\text{Benzamic acid.}}{\left.\begin{matrix}C_7H_4(NH_2)O\\H\end{matrix}\right\}O}+2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)+3S;$$

The constitution of the class of bodies to which benzamic acid belongs is still under discussion: they are generally viewed as monamines. Benzamic acid, according to this view, is formulated thus:— $\left.\begin{matrix}C_7H_5O_2\\H\\H\end{matrix}\right\}N$. Hofmann is of opinion that they may be equally well regarded as amidic acids (716), and that this latter view is supported by many important facts. Benzamic acid, viewed as an amidic acid, would be formulated thus:—$\left.\begin{matrix}(C_7H_4O)''H_2N\\H\end{matrix}\right\}O$. The student will see, by this example, that if these bodies are viewed as amidic acids, we must assume they contain a diatomic radical. (See also par. 717.)

687. If we heat to 50° or 60° C. a mixture of concentrated sulphuric acid and fuming nitric acid, then add by degrees, and only small fragments at a time, one of these acids, immediately a reaction is manifested by the disengagement of gas, and the solution of the acid. When the solution is complete, it is gently heated until the liquid commences to be troubled; water is then added to the acid liquid, and it is subsequently left to cool. A solid acid separates, which can be purified by crystallization from alcohol. This solid acid is a binitroacid, in which two atoms of hydrogen in the acid radical have been replaced by two atoms of NO_2. The basicity of the acid is not altered by this replacement; it is still monobasic.

688. When anhydrous sulphuric acid is brought into contact with the normal or monohydrated monobasic organic acids, one atom of SO_2 replaces one atom of hydrogen in the acid radical; the sulphoconjugated acid thus produced is bibasic; examples:—

$$\text{(1.)}\quad \overset{\text{Acetic acid.}}{\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O}+SO_2,O=\overset{\text{Sulphacetic acid.}}{\left.\begin{matrix}C_2H_2(SO_2)O\\H_2\end{matrix}\right\}O_2}$$

$$\text{(2.)}\quad \overset{\text{Benzoic acid.}}{\left.\begin{matrix}C_7H_5O\\H\end{matrix}\right\}O}+SO_2,O=\left.\begin{matrix}C_7H_4(SO_2)O\\H_2\end{matrix}\right\}O_2$$

689. These sulphoacids can also be formed by treating the amides or nitrides of the series with fuming sulphuric acid; examples:—

Butyramide.

$$(1.)\ C_4H_9NO+2\left(\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2\right)=\left.\begin{matrix}C_4H_6(SO_2)O\\H_2\end{matrix}\right\}O_2+\left.\begin{matrix}(NH_4)H\\(SO_2)''\end{matrix}\right\}O_2$$

Benzonitrile.

$$(2.)\ C_7H_5N+\left.\begin{matrix}H\\H\end{matrix}\right\}O+2\left(\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2\right)=\left.\begin{matrix}C_7H_4(SO_2)O\\H_2\end{matrix}\right\}O_2+\left.\begin{matrix}(NH_4)H\\(SO_2)''\end{matrix}\right\}O_2$$

690. If, after the addition of the sulphuric acid, the solution is heated, another series of sulphoacids, along with those we have just described, is formed; this second series contains two equivalents of SO_2, but only one equivalent of H has been removed; the introduction of the second equivalent is attended with the partial destruction of the original body, as the reaction is attended with the evolution of carbonic acid: Hofmann and Buckton, who have extended our knowledge of these compounds, consider they are compounds composed of a member of the marsh gas family with anhydrous sulphuric acid, and they term them *disulpho-acids*. We will contrast the reaction of fuming sulphuric acid on propionitrile in the formation of a sulphoacid, both of the first and second series.

First Series:—

Propionitrile.

$$C_3H_5N+\left.\begin{matrix}H\\H\end{matrix}\right\}O+2\left(\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2\right)=\left.\begin{matrix}C_3H_4(SO_2)O\\H_2\end{matrix}\right\}O_2+\left.\begin{matrix}(NH_4)H\\(SO_2)''\end{matrix}\right\}O_2$$

Second Series:—

Propionitrile.

$$C_3H_5N+3\left(\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2\right)=\left.\begin{matrix}C_2H_4(SO_2)_2\\H_2\end{matrix}\right\}O_2+CO_2+\left.\begin{matrix}(NH_4)H\\(SO_2)''\end{matrix}\right\}O_2$$

691. The anhydrides of these monobasic acids are obtained in the same ways as those of the first class.

692. *Oxidation of cuminic acid.*—If cuminic acid is boiled with a mixture of sulphuric acid and bichromate of potash, it becomes transformed into a bibasic acid, which has been designated insolinic acid; this new acid is

derived from cuminic acid by the oxidation of part of its carbon and hydrogen, oxygen being at the same time fixed.

$$\left.\begin{matrix}C_{10}H_{11}O\\H\end{matrix}\right\}O+6O=CO_2+2H_2O+\left.\begin{matrix}C_8H_4O_2\\H_2\end{matrix}\right\}O_2$$

This acid is noticed in its proper place amongst the bibasic acids. Attempts have been made to prepare corresponding acids, by the same treatment, from other members of the cuminic group, but hitherto without success.

693. *Changes by distillation.*—When the salts of any of the monobasic acids which contain two equivalents of oxygen are distilled with hydrate of baryta, they undergo decomposition, all the oxygen in the acid, along with as much carbon as is necessary to form carbonic acid, remain combined with the baryta in the retort as carbonate of baryta, whilst a hydrocarbon distils over; examples:—

Acetate of soda. Marsh gas.

$$(1.)\ 2\left(\left.\begin{matrix}C_2H_3O\\Na\end{matrix}\right\}O\right)+2\left(\left.\begin{matrix}Ba\\H\end{matrix}\right\}O\right)=2CH_4+\left.\begin{matrix}CO\\Na_2\end{matrix}\right\}O_2+\left.\begin{matrix}CO\\Ba_2\end{matrix}\right\}O_2$$

Benzole.

$$(2.)\ 2\left(\left.\begin{matrix}C_7H_5O\\Ca\end{matrix}\right\}O\right)+2\left(\left.\begin{matrix}Ba\\H\end{matrix}\right\}O\right)=2C_6H_6+\left.\begin{matrix}CO\\Ca_2\end{matrix}\right\}O_2+\left.\begin{matrix}CO\\Ba_2\end{matrix}\right\}O_2$$

694. Piria has obtained hydride of benzoyl by distilling benzoate of lime with formiate of lime; thus:—

Benzoate of lime. Formiate of lime. Hydride of benzoyl.

$$\left.\begin{matrix}C_7H_5O\\Ca\end{matrix}\right\}O+\left.\begin{matrix}CHO\\Ca\end{matrix}\right\}O=C_7H_5O,H+\left.\begin{matrix}CO\\Ca_2\end{matrix}\right\}O_2.$$

695. Miller, in his "Elements of Chemistry," suggests that the missing hydride (C_8H_7O,H) would probably be obtained by distilling toluate of lime with formiate of lime.

FIFTH CLASS.

(*General formula,* $\left.\begin{matrix}C_nH_{2n-11}O\\H\end{matrix}\right\}O.$)

696. Only one acid (cinnamic acid) belonging to this class is yet known; the formula of the acid is $\left.\begin{matrix}C_9H_7O\\H\end{matrix}\right\}O$; it resembles in its physical characters the acids of the fourth class; it is solid and crystalline; it sublimes and is little soluble in cold, but soluble in hot water. This acid

is contained in many balsams, such as those of storax, of tolu, and of Peru; it can be prepared artificially by heating its aldehyde with hydrate of potash, thus:—

Hydride of cinnamyl.

$$C_9H_7O,H+\left.\begin{matrix}K\\H\end{matrix}\right\}O=\left.\begin{matrix}C_9H_7O\\K\end{matrix}\right\}O+HH$$

697. The chemical properties of this acid are very analogous to those of the preceding class. By the action of chlorine, bromine, nitric acid, and sulphuric acid, similar compounds are produced. When submitted to the reducing action of hydrogen, nitro-cinnamic acid yields a similar amidic body; it also yields, by distillation with hydrate of lime or baryta, a corresponding hydrocarbon.

698. We have already noticed, that cinnamyl compounds stand in the same relation to the preceding class as the allylic to the acetic series (501); the following reactions indicate also the close relation which exists between cinnamic and benzoic acids. (1.) If cinnamic acid be distilled with bichromate of potash and sulphuric acid, it yields hydride of benzoyl. (2.) When fused with an excess of hydrate of potash, it is resolved into acetic and benzoic acids, whilst hydrogen is liberated.

Cinnamic acid. Acetate of potash. Benzoate of potash.

$$\left.\begin{matrix}C_9H_7O\\H\end{matrix}\right\}O+2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)=\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O+\left.\begin{matrix}C_7H_5O\\K\end{matrix}\right\}O+HH$$

SIXTH CLASS.

(*General formula*, $\left.\begin{matrix}C_nH_{2n-9}O_2\\H\end{matrix}\right\}O.$)

699. Only two acids belonging to this class are as yet known; they resemble, in their physical characters, the acids of the fourth class; they are solid and crystalline, they sublime, and are little soluble in cold water. The following are the names and formulæ of the two acids:—

Salicylic acid $\left.\begin{matrix}C_7H_5O_2\\H\end{matrix}\right\}O$. Anisic acid $\left.\begin{matrix}C_8H_7O_2\\H\end{matrix}\right\}O$

700. These acids contain the same proportion of carbon and hydrogen as the acids of the fourth group, but they contain one atom more oxygen than the acids in that group; they therefore stand in the same relation to the members of that class as nitric acid does to nitrous.

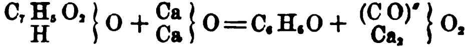
701. The only known natural compound of salicylic

acid is the oil of winter green, which is the methyl compound of this acid; the acid can be prepared artificially by heating salicylous acid with an excess of solid hydrate of potash, or by fusing salicin with an excess of that reagent. Anisic acid can be prepared from its aldehyde by boiling with caustic potash.

702. The chemical as well as physical properties of these acids resemble those of the fourth class. By the action of chlorine, bromine, nitric, and sulphuric acids, similar substitution compounds can be obtained. The nitro-compounds, when reduced by hydrogen, yield similar amidic bodies.

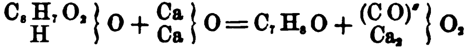
703. But when distilled with baryta or lime, they yield, from their containing another equivalent of oxygen, oxidized bodies, whereas we have seen that the acids containing two equivalents of oxygen yield hydrocarbons; thus:—

Phenic acid.



$$\left.\begin{matrix} C_7H_5O_2 \\ H \end{matrix}\right\} O + \left.\begin{matrix} Ca \\ Ca \end{matrix}\right\} O = C_6H_6O + \left.\begin{matrix} (CO)'' \\ Ca_2 \end{matrix}\right\} O_2$$

Anisole.



$$\left.\begin{matrix} C_8H_7O_2 \\ H \end{matrix}\right\} O + \left.\begin{matrix} Ca \\ Ca \end{matrix}\right\} O = C_7H_8O + \left.\begin{matrix} (CO)'' \\ Ca_2 \end{matrix}\right\} O_2$$

Anisole has the composition of phenate of methyl, $C H_3 O, C_6 H_5 O$; Cahours has actually formed phenate of methyl synthetically by decomposing iodide of methyl with phenate of potash.

704. It would perhaps have been more appropriate to have placed this class of acids in the biatomic group, as there can be no doubt that salicylic acid is at least biatomic if not bibasic, resembling lactic acid in this respect; and anisic acid must also be biatomic.

APPENDIX C.

705. Professor Brodie has recently obtained the peroxides of benzoyl and acetyl, or othyl, by acting upon the acid anhydrides of those bodies, or upon their corresponding chlorides, with peroxide of barium. These peroxides stand in the same relation to acids, and the hydrated acids, as peroxide of hydrogen stands to water. The formula for peroxide of benzoyl is $C_{14} H_{10} O_4$, and the formula for peroxide of acetyl is $C_4 H_6 O_4$. They, like peroxide of hydrogen, easily decompose.

(3.) OXYGEN SALTS.

706. *Definition of an oxygen salt.*—An oxygen salt may be viewed as water in which a part of the hydrogen is replaced by an acid radical, and the other part is entirely or partially replaced by a metal, or other positive radical. We have already defined acids proper as bodies in which one half the hydrogen in water is replaced by an acid radical; it is therefore the typical hydrogen in the acid which, in the formation of an oxygen salt, becomes replaced by a metal, or positive radical. Acids with only one atom of typical hydrogen are necessarily monobasic. Acids with two atoms of typical hydrogen are generally bibasic. As in bibasic acids the two atoms can be replaced by metals, or other positive radicals, a bibasic acid can form two classes of salts; one class consisting of the *neutral* or *normal* salts of the acid—salts in which all the typical hydrogen has been replaced by a metal or other positive radical; the other class consisting of acid salts—salts in which only one atom of the typical hydrogen is replaced, the other atom remaining. "In the same manner, acids with three and four atoms of hydrogen respectively, are usually tri- and tetra-basic, and form, each, in addition to their neutral or normal salts, two and three varieties of acid salts. Thus, arsenic acid, $H_3 As O_4$, forms normal arsenate of sodium, $Na_3 As O_4$, and two descriptions of acid arsenates, $Na_2 H As O_4$ and $Na H_2 As O_4$ respectively. Acid salts constitute, to all intents and purposes, a variety of the class of acids; and for the most part react with vegetable colours, and alkaline hydrates and carbonates, as do the normal acids, although, indeed, there are many exceptions."

707. When there are two or three different varieties of an acid, as in the case of phosphoric acid, the common one is termed the ortho-acid; ortho-phosphoric acid means, for instance, tribasic phosphoric acid, and its different salts are called the ortho-phosphates.

708. There are sulphur salts as well as oxygen salts; the sulphur salts are formed from the type of $\left.\begin{matrix}H\\H\end{matrix}\right\} S$; with this exception, the definition we have given of an oxygen salt applies also to a sulphur salt.

SALTS OF THE MONOBASIC INORGANIC ACIDS.

EXERCISE.

147. Write out the formula for nitrate of potassium, for metaphosphate of sodium, for chlorate of potassium, for nitrate of silver, for hypochlorite of calcium.

SALTS OF THE MONOBASIC ORGANIC ACIDS.

709. We may here state, for the information of the student, that the soluble and insoluble salts of the organic acids are produced by methods similar to those by which the soluble and insoluble salts of the inorganic acids are prepared.

EXERCISE.

148. Write out the formulæ for the following salts:—Formiate of lead, acrylate of potassium, cinnamate of copper, sorbate of silver, cumate of barium, benzoate of sodium, valerate of copper, acetate of barium, thiobutyrate of sodium, bromopropionate of calcium, quadrichlorbutyrate of potassium, binitrobenzoate of silver, toluate of copper, thiacetate of lead, oleate of sodium, caprate of magnesium, nitrocuminate of zinc; caprylate of sodium, chloracetate of potassium, elaidate of silver, cerotate of lead, melissate of ammonium.

(4.) COMPOUND ETHERS.

710. *Definition of compound ethers.*—When the basic or typical hydrogen of an acid is replaced by an alcohol radical, the compound is termed a compound ether. Monobasic acids form but one compound ether; bibasic acids form two, a neutral and an acid ether; and tribasic acids, one neutral and two acid ethers. The acid ethers, called also vinic acids, are true acids, and form salts. The neutral ethers are generally liquid or solid bodies, volatile, without decomposition, more or less odorous, little soluble in water, soluble in alcohol, and without action upon test-papers. Considered under the same volume, in the state of vapour, the neutral ethers contain one, two, or three times the alcohol radical, according as they correspond to a monobasic, bibasic, or tribasic acid. The acid ethers are generally very soluble in water, and without odour; they turn blue litmus red, decompose the carbonates with effervescence, are not volatile without decomposition, and form salts which are, generally, very soluble in water.

711. Generally, the compound ethers do not present, in ordinary circumstances, the reactions proper to the acids the radicals of which they contain. Thus, sulphate of methyl does not precipitate salts of baryta, like the metallic sulphates; but by prolonged contact with water, the ether compounds are decomposed into the acid and alcohol, and then the acid gives its characteristic reactions. This decomposition of compound ethers into their acids and alcohols is effected promptly by boiling them with potash; the acid of the ether combines with the potash, whilst the alcohol distils off; certain energetic mineral acids, as sulphuric and hydrochloric acids, determine also the same transformation. Each compound ether can always be recognised from the acid and the alcohol into which it is thus converted.

712. Many of the compound ethers are converted by ammonia into an amide and alcohol.

713. Under the influence of chlorine the compound ethers give conjugated derivatives.

MONATOMIC ETHERS.

714. They are derived from one molecule of water, correspond to the monobasic acids, and are always neutral. They are liquid or solid bodies, volatile, without decomposition. They are produced by the following different methods:—

(1.) By the solution of an acid anhydride in alcohol.

$$\left.\begin{matrix} C_7H_5O \\ C_7H_5O \end{matrix}\right\} O + \left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\} O = \left.\begin{matrix} C_7H_5O \\ C_2H_5 \end{matrix}\right\} O + \left.\begin{matrix} C_7H_5O \\ H \end{matrix}\right\} O$$

(2.) Some organic acids (benzoic, butyric, palmitic) produce compound ethers when they are heated to 360° or 400° C., in closed tubes with ether.

(3.) In some cases the compound ether can be obtained by heating the hydrated acid and the alcohol together; the formation of the ether can be considerably hastened, in the majority of these cases, by adding sulphuric acid along with the acid and alcohol, and then distilling.

(4.) By the distillation of a metallic salt of the acid with alcohol and sulphuric acid; or by distilling the acid and a sulphovinate together; or a salt of the acid and a sulphovinate, thus:—

$$\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O+\left.\begin{matrix}SO_2\\C_2H_5\\K\end{matrix}\right\}O_2=\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}O+\left.\begin{matrix}SO_2\\K_2\end{matrix}\right\}O_2$$

(5.) By the action of a salt of silver and hydriodic ether, thus:—

$$\left.\begin{matrix}C_2H_3O\\Ag\end{matrix}\right\}O+C_2H_5I=\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}O+AgI.$$

(6.) By the action of the chloride of an acid radical and alcohol, thus:—

$$C_7H_5O,Cl+\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O=HCl+\left.\begin{matrix}C_7H_5O\\C_2H_5\end{matrix}\right\}O$$

(7.) By passing dry hydrochloric acid gas into a solution of the acid in absolute alcohol.

715. The boiling point of a monatomic ether is lower than the boiling point of its monobasic acid; a methylic ether is about 63° C. lower than the corresponding acid, and an ethylic ether is about 44° C. lower.

EXERCISE.

149. Write out the formulæ for the following ethers:—Nitrate of methyl, chloric ether, benzoate of allyl, palmitic ether, enanthylate of phenyl, chloronitrobenzoate of ethyl, valerate of amyl, bibromobutyric ether, stearic ether, acrylic ether, formiate of butyl, angelic ether, caproate of amyl, acetate of capryl, caprylate of methyl, palmitate of cetyl, cerotate of ceryl, laurate of ethyl.*

(5.) ACID DERIVATIVES OF AMMONIUM, CONSTRUCTED ON THE WATER TYPE.†

716. The hydrogen in hydrated oxide of ammonium can be replaced by acid radicals; the bodies thus produced have acid properties; they have been designated *amidogen acids*, or *amic* or *amidic* acids. Almost all the amidogen acids yet known are constructed on the simple molecule; a few are known which are constructed on the

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* The student must now go back to page 269; first, write out answers to the exercises on that page, and then study the polymolecular groups; commencing at par. 513, and ending at par. 540. He then passes to par. 726, page 336, and thence forward.

† This group of acids must be passed over until the student has gone through the following groups:—(1) monamines, (2) monamides, (3) the haloid salts of the monammoniums, (4) the hydrated oxides of the monammoniums.

type of a double molecule of hydrated oxide of ammonium; but none have yet been formed on the treble molecule.

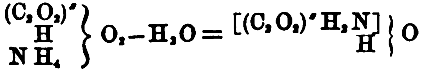
MONAMIDIC ACIDS.

717. The monamidic acids, according to the number of hydrogen equivalents replaced, may be subdivided into secondary, tertiary, and quartary acids; primary monamidic acids have never been obtained; it is only when two or more equivalents of hydrogen in the ammonium molecule have been replaced by acid molecules, of which one must be diatomic, that monamidic acids appear capable of existing.

SECONDARY MONAMIDIC ACIDS.

718. Secondary monamidic acids are produced by the replacement of two atoms of hydrogen in one ammonium molecule, by one atom of the acid radical of a dibasic acid; they therefore contain the elements of one equivalent of water *less* than the acid ammonium salts of dibasic acids; example:—

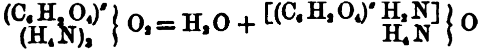
Acid oxalate of ammonium. Oxamic acid.



$$\left.\begin{array}{c}(C_2O_2)''\\H\\NH_4\end{array}\right\}O_2-H_2O=\left.\begin{array}{r}[(C_2O_2)''H_2N]\\H\end{array}\right\}O$$

719. *Formation of these acids.*—(1.) In many cases they can be formed by simply driving off by heat one atom of water from the acid ammonium salts of the bibasic acids.—(2.) Sometimes it is sufficient to boil the solution of the ammonium compound, for instance.

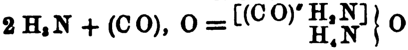
Comenate of ammonium. Comenamate of ammonium.



$$\left.\begin{array}{c}(C_6H_2O_4)''\\(H_4N)_2\end{array}\right\}O_2=H_2O+\left.\begin{array}{r}[(C_6H_2O_4)''H_2N]\\H_4N\end{array}\right\}O$$

(3.) They may also be obtained by acting upon the anhydride of a dibasic acid with dry ammonia in excess; the two bodies combine together; the compound which is produced is the ammonium salt of the acid.

Carbamate of ammonium.



$$2\,H_3N+(CO)''\,O=\left.\begin{array}{r}[(CO)''H_2N]\\H_4N\end{array}\right\}O$$

(4.) The acid ethers of some dibasic acids, when treated with ammonia, also yield these acids.

(5.) "These acids may also be conveniently produced by the action of water upon the secondary amides, containing a diatomic acid radical, which are often designated as imides. Instead of the imide, one of its metallic derivatives may be employed. The reaction, which consists in the assimilation of one equivalent of water, is generally accomplished by boiling the amide with ammonia, and occasionally with carbonate of sodium.

Succinyl-argent-amide. Succinamate of silver.

$$\left.\begin{array}{r}(C_4H_4O_2)''\\ Ag\end{array}\right\} N + H_2O = \left.\begin{array}{r}[(C_4H_4O_2)''H_2N]\\ Ag\end{array}\right\} O$$

(6.) "By a similar fixation of one equivalent of water, many primary diamides are converted into the ammonium compounds of these acids. In this manner, asparagin (malamide) is converted into aspartate (malamate) of ammonium.

Asparagin. Aspartate of ammonium.

$$\left.\begin{array}{r}(C_4H_4O_3)''\\ H_2\\ H_2\end{array}\right\} N_2 + H_2O = \left.\begin{array}{r}[(C_4H_4O_3)''H_2N]\\ H_4N\end{array}\right\} O$$

(7.) "Lastly, some peculiar reactions may be mentioned, in which the ethers of the amidic acids are formed.

"Chlorocarbonate of ethyl, when treated with ammonia, yields carbamate of ethyl, generally called *urethane*.

$$\left.\begin{array}{l}(CO)''\\ (C_2H_5)\end{array}\right\} \begin{array}{l}O\\ Cl\end{array} + 2\,H_3N = \left.\begin{array}{r}[(CO)''H_2N]\\ C_4H_5\end{array}\right\} O + H_4N\,Cl$$

"Oxalate of ethyl gives, with a small quantity of alcoholic ammonia, oxamate of ethyl (oxamethane).

$$\left.\begin{array}{l}(C_2O_2)''\\ (C_2H_5)_2\end{array}\right\} O_2 + H_3N = \left.\begin{array}{r}[(C_2O_2)''H_2N]\\ C_2H_5\end{array}\right\} O + \left.\begin{array}{r}C_2H_5\\ H\end{array}\right\} O$$

EXERCISE.

150. Write out the formulæ for the following substances:—Carbamate of ammonium, sulphocarbamic acid, sulphamic acid, oxamate of baryta, sebamate of ammonium, succinnamate of silver, camphoramic acid, malamic acid (aspartic acid).

720. The salts of this class of amidic acids are generally more soluble than the salts of the same base with these bibasic acids.

721. Many of these amidic acids lose water at an

elevated temperature, and are transformed by this loss into imides.

722. Boiled with acids or alkalies, these acids fix water, and form acid ammonium salts.

TERTIARY MONAMIDIC ACIDS.

(1.) *Substitution of one monatomic and one diatomic acid radical.*

723. This class of tertiary acids is formed by the action of monatomic acid chlorides upon secondary amidic acids.

$$\overset{\text{Salicylamic acid.}}{\left.\begin{matrix}[(C_7H_4O)''H_2N] \\ H\end{matrix}\right\}O} + \overset{\text{Chloride of benzoyl.}}{(C_7H_5O)Cl} =$$

$$\overset{\text{Salicyl-benzamic acid.}}{\left.\begin{matrix}\left[\begin{matrix}(C_7H_4O)'' \\ (C_7H_5O)\end{matrix}\ HN\right] \\ H\end{matrix}\right\}O} + HCl$$

(2.) *Substitution of one diatomic acid radical and one monatomic alcohol radical.*

724. This class may be formed:—(1.) By substituting a monamine in place of ammonia in the acid ammoniacal salt, and submitting these salts to heat, we obtain, in place of the secondary amidic acids, which we have seen are formed when acid ammonium salts are thus treated, a tertiary monamine of this class.

$$\left.\begin{matrix}(C_2O_2)'' \\ H \\ [(C_2H_5)H_3N]\end{matrix}\right\}O_2 - H_2O = \overset{\text{Ethyl-oxamic acid.}}{\left.\begin{matrix}[(C_2O_2)''(C_2H_5)HN] \\ H\end{matrix}\right\}O}$$

(2.) They may also be formed by the action of the anhydrides of dibasic acids upon the primary monamines, a salt of the amidogen acid and the monamine being formed.

$$2\left(\left.\begin{matrix}C_5H_{11} \\ H \\ H\end{matrix}\right\}N\right) + (CS)''S = \overset{\text{Amyl-sulphocarbamate of amylamine.}}{\left.\begin{matrix}[(CS)''(C_5H_{11})HN] \\ [(C_5H_{11})H_3N]\end{matrix}\right\}S}$$

(3.) By the action of water upon tertiary monamides, containing a diatomic acid radical, and a monatomic alcohol radical.

"The largest number of tertiary amidic acids has been procured by this process, which is conveniently accomplished by ebullition with ammonia."

Phenyl-succinimide. Phenyl-succinamic acid.

$$\left.\begin{matrix}(C_4H_4O_2)''\\(C_6H_5)\end{matrix}\right\}N + H_2O = \left[(C_4H_4O_2)''(C_6H_5)H\begin{matrix}N\\H\end{matrix}\right\}O$$

EXERCISE.

151. Write out the formulæ for the following substances:—Phenyl-carbamic acid (anthranilic acid), phenyl-sulphamic acid (sulphanilic acid), phenyl-succinamic acid (succinanilic acid), phenyl-malamic acid (malanilic acid).

725. As there are very few members yet known belonging to the class of quartary monamidic acids, we shall pass them over without further notice.

DOUBLE MOLECULE.

$$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$$

POSITIVE GROUP.

726. This group embraces—(1) The metallic derivatives of water. (2) The basic derivatives of ammonium constructed on the double molecule of water. (3) The biatomic alcohols. (4) Polyethylenic bodies. (5) The aldehydes, as isomers of the glycols.

(1.) HYDRATES OF THE METALS PROPER (PRIMARY DERIVATIVES). ANHYDROUS OXIDES (SECONDARY DERIVATIVES).

727. *Primary derivatives.*—The biatomic metals which are given under the double molecule of hydrogen (H_2H_2), form hydrates on the type of a double molecule of water; the general formula of these hydrates is, therefore, $\left.\begin{matrix}M''\\H_2\end{matrix}\right\}O_2$.

728. *Secondary derivatives.*—The general formula of the anhydrous oxides of the biatomic metals is $\left.\begin{matrix}M''\\M''\end{matrix}\right\}O_2$.

729. The sulphides, &c., of the biatomic metals are, of course, constructed on the type of a double molecule of water, in which the oxygen is replaced by sulphur.

730. There are some combinations of these biatomic metals with the alkaline metals and oxygen, which may be regarded as constructed on the double molecule of water, in which two of the atoms of water are replaced by one equivalent of the biatomic metal, and the other two

equivalents by two equivalents of the alkaline metals. Examples: $\left.\begin{matrix}Pt'\\K_2\end{matrix}\right\}O_2$ (platinite of potassium) $\left.\begin{matrix}Sn'\\Na_2\end{matrix}\right\}O_2$ (stannite of sodium).

731. Such bodies as chrome iron ore, brown hæmatite, magnetic oxide of iron, and bismuthite of sodium, may be regarded as constructed on the double molecule of water, in which three atoms of the hydrogen are replaced by two atoms of a sesquiatomic metal, or one atom of a teratomic metal, the other atom of hydrogen remaining, or being substituted by a monatomic metal. Examples:—

$\left.\begin{matrix}Ffe'''\\H\end{matrix}\right\}O_2$, brown hæmatite.

$\left.\begin{matrix}Ffe'''\\Fe'\end{matrix}\right\}O_2$, magnetic oxide of iron.

$\left.\begin{matrix}Ccr''\\Fe'\end{matrix}\right\}O_2$, chrome iron ore.

732. The indifferent binoxides—or peroxides, as they are frequently called—may be represented on the type of a *single molecule of water*, by supposing one-half the oxygen to be associated with the positive radical, thus:—

Peroxide of hydrogen - - -	$\left.\begin{matrix}HO\\H\end{matrix}\right\}O$
Peroxide of manganese - - -	$\left.\begin{matrix}MnO\\Mn\end{matrix}\right\}O$
Peroxide of lead - - - - -	$\left.\begin{matrix}PbO\\Pb\end{matrix}\right\}O$

(2). THE BASIC DERIVATIVES OF AMMONIUM, CONSTRUCTED ON THE TYPE OF A DOUBLE[*] MOLECULE.

733. We shall only give here a few exercises for the student to write, as the formation of the bodies is fully explained in the introduction to the polyammonias.

EXERCISE.

152. Write out the formulæ of the following bodies:— Hydrated oxide of triethyl-ethylene diammonium; hydrated

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[*] The exercises in this group of ammonium derivatives must not be attempted until the student has passed through the following groups:—(1) diamines; (2) diamides; (3) the haloid salts of the diammoniums.

oxide of hexethyl-ethylene diphosphonium; hydrated oxide of triethyl-ethylene phosphammonium; hydrated oxide of hexethyl-ethylene arsonium; hydrated oxide of trimethyl-triethyl-ethylene phosphammonium; hydrated oxide of triethyl-ethylene arsammonium; hydrated oxide of hexethyl-ethylene phospharsonium; hydrated oxide of tetrethyl-ethylene phosphammonium.

(3.) BIATOMIC ALCOHOLS, OR GLYCOLS.

(*General formula,* $\left.\begin{matrix}(C_n H_{2n})' \\ H_2\end{matrix}\right\} O_2$.)

734. These alcohols are constituted on the type of a double atom of water; two out of the four atoms of hydrogen in the two atoms of water are replaced by one atom of a diatomic radical, whilst the other two atoms remain. Only one group of this class of alcohols is at present known; and only four members belonging to the group have been produced; but the student will see that this number could easily be extended. The diatomic radical which replaces the hydrogen, is a member of the olefiant gas series.*

735. The following is a list of these alcohols which have yet been produced. The student ought to commit to memory their names and symbols:—

	Boiling Point.	
Glycol (ethylic) -	- 387° F. -	$\left.\begin{matrix}(C_2 H_4)' \\ H_2\end{matrix}\right\} O_2$
Propyl-glycol -	- 372 - -	$\left.\begin{matrix}(C_3 H_6)' \\ H_2\end{matrix}\right\} O_2$
Butyl-glycol -	- 361 - -	$\left.\begin{matrix}(C_4 H_8)' \\ H_2\end{matrix}\right\} O_2$
Amyl-glycol -	- 350 - -	$\left.\begin{matrix}(C_5 H_{10})' \\ H_2\end{matrix}\right\} O_2$

736. *Physical Properties.*—These bodies are syrupy liquids, volatile without decomposition, and soluble in

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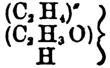
* Quite recently, ethylic glycol has been obtained from vinic alcohol. The bromide of monobromide of ethyl $(C_2 H_4 Br)'$ Br, which is isomeric with bibromide of ethylene $(C_2 H_4)''$ Br_2, was digested with acetate of silver, when diacetate of glycol was produced, which yielded, when treated with potash, glycol. The student will see by this example that monatomic alcohols can be converted into biatomic ones by employing brominated monatomic radicals. He will learn, further on, that monatomic acids can be converted into biatomic ones, and that two, three, four or more atoms of ammonia can be made to coalesce by employing brominated bodies.

water and vinic alcohol, but only slightly soluble in ether. In these respects they resemble the triatomic alcohol glycerin. In their solvent properties they stand between water and vinic alcohol; and in their chemical properties they present, as we shall presently see, the closest relationship with the first class of monatomic alcohols. We have seen that the boiling points of the monatomic alcohols increase by about 33° F. for each additional increment of $C H_2$; but these diatomic alcohols display in this respect a very remarkable difference, for the boiling points of these bodies decrease with each increment of $C H_2$.

737. *Preparation.*—We have already noticed the way Wurtz prepared glycol (par. 518), viz., by acting upon iodide of ethylene with acetate of silver, and decomposing the diacetate of glycol thus formed by potash. But the best plan for preparing glycol is that proposed by Dr. Atkinson. It consists in heating an alcoholic solution of one atom of bromide of ethylene with two atoms of acetate of potash, inclosed in a soda-water bottle, for two days, at 212° F. The liquid is separated from the bromide of potassium, subjected to distillation, and those portions are collected as monacetate of glycol,  $\left.\begin{matrix}(C_2 H_4)''\\(C_2 H_3 O)\\H\end{matrix}\right\} O_2$, which come over about 356° F. To obtain the glycol, the monacetate is mixed with an equivalent quantity of potash, which decomposes it with evolution of heat. The mixture, after having been allowed to stand for some time, is distilled in the oil bath. On rectifying the distillate, a product is obtained, boiling at 387° F., which is pure glycol. In a similar manner the other three glycols have been obtained.*

738. *Chemical Properties.*—In studying the deportment of these biatomic bodies with reagents, we must constantly remember that they are constructed upon the type of two atoms of water, and that the two hydrogen atoms which remain are capable of being replaced by simple and compound radicals. Two series of bodies can,

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* Debus found that Atkinson's plan only yielded one-half the calculated quantity of glycol. He has, therefore, modified the process. By this modification, a larger quantity of glycol is obtained from a given quantity of material. The student will find the process described in vol. xiii., page 422, of Gmelin's "Handbook of Chemistry."

on this account, be obtained with these diatomic alcohols, whilst only one series can be obtained from the monatomic alcohols, on account of their only containing one replaceable atom of hydrogen. We will commence by studying the replacement of these hydrogen atoms by simple and compound electro-positive radicals.

739. *Substitution of other electro-positive bodies for the typical hydrogen.*—In contact with potassium or sodium, ethylo-glycol loses one or two atoms of hydrogen, which are replaced by the metal. Example:—Monosodium glycol, $\left.\begin{matrix}(C_2H_4)''\\ Na\,H\end{matrix}\right\}O_2$, and bisodium glycol, $\left.\begin{matrix}(C_2H_4)''\\ Na_2\end{matrix}\right\}O_2$. Iodide of ethyl and these sodium compounds react upon one another, and we get bodies in which one or both atoms of the hydrogen of the glycol are replaced by ethyl. Thus, monethyl-glycol, $\left[\left.\begin{matrix}(C_2H_4)''\\ (C_2H_5)H\end{matrix}\right\}O_2\right]$, and diethyl-glycol, $\left[\left.\begin{matrix}(C_2H_4)''\\ (C_2H_5)_2\end{matrix}\right\}O_2\right]$. If potassium is added to monethyl-glycol, the hydrogen of the water is replaced by the metal. Example: $\left[\left.\begin{matrix}(C_2H_4)''\\ (C_2H_5)K\end{matrix}\right\}O_2\right]$.

740. Wurtz at first considered that the ethers of these biatomic alcohols would stand in the same relation to their alcohols as the ethers derived from the monatomic alcohols stand in relation to their alcohols. If this were the case, the general formula of these ethers would be $\left.\begin{matrix}(C_nH_{2n})''\\ (C_nH_{2n})''\end{matrix}\right\}O_2$; he therefore attempted to form ethylene ether by acting upon bisodic glycol with bibromide of ethylene, but the only products were bromide of aldehydene and glycol. He then attempted it by acting upon monosodium glycol with bromide of aldehydene, but the products obtained were chiefly olefiant gas and glycol. Wurtz was also at one time of opinion that the aldehydes were the true ethers of the glycols, because glycol, treated with chloride of zinc, yields aldehyde; but that body does not reproduce glycol when treated with water, or compound glycolic ethers when treated with acids. We shall presently consider the composition and formation of the true ethers of these biatomic alcohols.

741. *Substitution of electro-negative bodies for the hydrogen.*—If glycol and hydrochloric acid are heated

together, water and chlorhydrine of glycol (chlorhydrate of oxide of ethylene) are formed. The formula of this latter body is $\left.\begin{matrix}(C_2H_4)''\\H\\Cl\end{matrix}\right\}O$. We have said that, on account of the two replaceable atoms of hydrogen in these compounds, two series of compounds could be formed. This body is an example of the first series of compounds formed in the conversion of these alcohols into their normal chlorides ($C_nH_{2n}Cl_2$), the first stage in the conversion of a body constructed on the type of two atoms of water into one constructed on the type of two atoms of hydrochloric acid; regarded as constructed on the type of water, it is only constructed on one atom. This change is due to the substitution of one atom of chlorine for its equivalent of hydrogen; but this removal of the hydrogen is attended with the removal of an atom of oxygen; therefore peroxide of hydrogen, or the residue of water, has been replaced by chlorine. The following equation expresses the reaction:—

$$\left.\begin{matrix}(C_2H_4)''\\H\\H\end{matrix}\right\}O_2 + HCl = \left.\begin{matrix}(C_2H_4)''\\H\\Cl\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

742. If chlorhydrine of glycol were acted upon by hydrochloric acid, or by pentachloride of phosphorus, no doubt the true hydrochloric ether of glycol (dichloride of ethylene) $C_2H_4Cl_2$, would be formed. We have already seen (519) that this body is prepared from glycol by acting upon it with pentachloride of phosphorus.

743. Sulphuric acid, which is bibasic, and, like glycol, is derived from two atoms of water, yields similar derivatives:—

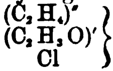
Sulphuric acid.	Glycol.
$\left.\begin{matrix}(SO_2)''\\H\\H\end{matrix}\right\}O_2$	$\left.\begin{matrix}(C_2H_4)''\\H\\H\end{matrix}\right\}O_2$
Intermediate compound.	Intermediate compound.
$\left.\begin{matrix}(SO_2)''\\H\\Cl\end{matrix}\right\}O$	$\left.\begin{matrix}(C_2H_4)''\\H\\Cl\end{matrix}\right\}O$

Dichloride of sulphuryle.	Dichloride of ethylene.
$(S O_2)'' Cl_2$	$(C_2 H_4)'' Cl_2$

744. Iodhydrine of glycol and diniodide of ethylene and bromhydrine of glycol and bibromide of ethylene can also be obtained, and in a similar manner.

745. It is evident there will also be two series of compounds when the hydrogen is replaced by compound monatomic acid radicals. The first will consist of the replacement of one of the atoms of hydrogen by one atom of the monatomic acid radical. The second series will consist of the replacement of the two atoms of hydrogen by two atoms of the acid radical. These two series are distinguished by the prefixes *mon* and *di*, as monacetate of glycol, diacetate of glycol. The monocompounds can not only be prepared by acting upon the bibromide of the biatomic radical with a salt of potash, but also by heating together equivalent quantities of glycol and the anhydrous acid. The dicompounds are formed by acting on the bibromide of the radical with a salt of silver.

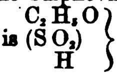
746. We can replace one atom of hydrogen by a compound monatomic acid radical, and the other atom by chlorine, bromine, or iodine; as in the formation of the chlorhydrine an atom of oxygen is removed with the hydrogen. Dr. Simpson obtained chlor-acetine of glycol,



$$\left.\begin{matrix}(C_2 H_4)'' \\ (C_2 H_3 O)' \\ Cl\end{matrix}\right\} O,$$

by heating a mixture of glycol, hydrochloric and acetic acids.

747. The glycols produced with polyatomic acid bodies are analogous to the sulphovinic acids. The formula of sulphoglycolic acid is



$$\left.\begin{matrix}C_2 H_5 O \\ (S O_2) \\ H\end{matrix}\right\} O_2:$$

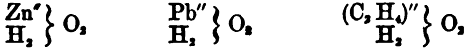
it is monobasic.

748. *Action of chloride of zinc.* — Chloride of zinc abstracts the elements of water from ethylic and propylic glycol, and converts the one into acetic, the other into propylic, aldehyde.

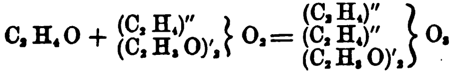
749. *Formation of the ethers of the glycols.*—Chlorhydrine of glycol is instantaneously decomposed by a solution of potash, chloride of potassium is formed, and an inflammable vapour is disengaged. This body is oxide of ethylene, $C_2 H_4 O$: its formation is easily explained. It is isomeric with aldehyde, from which it is distinguished

by some of its properties, and in some of its properties it resembles that body. Like aldehyde, it dissolves in water in all proportions; and it combines, like aldehyde, with bisulphite of soda, forming deliquescent crystals; but when mixed with ammoniacal ether, it does not form those well-known crystals which characterize aldehyde. It boils at 13·5° C., and aldehyde boils at 21° C.

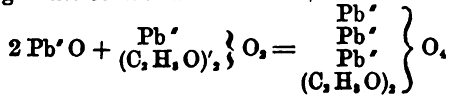
750. Oxide of ethylene possesses basic properties. Its basic properties are manifested by its action upon saline solutions, and by its combinations with acids. When it is mixed with a concentrated solution of chloride of magnesium, after some hours' boiling, the liquid solidifies, the magnesia is precipitated, and chlorhydrine of glycol is formed. The oxide, we have seen, is separated from this chlorine compound by potash. Heated in a salt bath, with a solution of perchloride of iron, it precipitates the hydrate of the sesquioxide of iron. Under the same circumstances, it precipitates alumina from a solution of alum, and subsulphate of copper from a solution of the sulphate. These experimental facts prove that it is comparable to the anhydrous oxides of zinc and lead, whilst glycol is in the same manner comparable to the hydrates of these oxides.


$$\left.\begin{matrix}Zn''\\H_2\end{matrix}\right\}O_2 \qquad \left.\begin{matrix}Pb''\\H_2\end{matrix}\right\}O_2 \qquad \left.\begin{matrix}(C_2H_4)''\\H_2\end{matrix}\right\}O_2$$

It combines directly with hydrochloric acid, and neutralizes it: the product formed is chlorhydrine of glycol. It combines directly with acetic acid, and also with acetic anhydride. The combination takes place slowly at the ordinary temperature, rapidly if heated, acetic glycol being produced. It even forms, like oxide of lead, basic acetates; for it is capable of combining with diacetate of glycol, and forming the acetate of diethylene, thus:—


$$C_2H_4O + \left.\begin{matrix}(C_2H_4)''\\(C_2H_3O)'_2\end{matrix}\right\}O_2 = \left.\begin{matrix}(C_2H_4)''\\(C_2H_4)''\\(C_2H_3O)'_2\end{matrix}\right\}O_3$$

This reaction is comparable to that which transforms the acetate of lead into basic acetate, when the neutral salt is brought into contact with an excess of oxide of lead:—


$$2\,Pb'O + \left.\begin{matrix}Pb'\\(C_2H_3O)'_2\end{matrix}\right\}O_2 = \left.\begin{matrix}Pb'\\Pb'\\Pb'\\(C_2H_3O)_2\end{matrix}\right\}O_4$$

The acetate of diethylene, and even the acetate of triethylene, $\left.\begin{matrix}(C_2H_4)'' \\ (C_2H_4)'' \\ (C_2H_4)'' \\ (C_2H_3O)'_2\end{matrix}\right\} O_4$, has been obtained by heating acetic acid and oxide of ethylene together. We shall refer again to these bodies.

751. Oxide of ethylene combines directly with water, glycol being produced. The direct formation of glycol from oxide of ethylene, and the basic character of the oxide, show that it is the true ether or anhydride of glycol, and, consequently, that the anhydrides of the biatomic alcohols contain the same number of carbon atoms as the alcohols themselves, and are derived from them by elimination of water, resembling, in this respect, the anhydrides of bibasic acids. For example:—

$$\left.\begin{matrix}(C_2H_4)'' \\ H_2\end{matrix}\right\} O_2 - \left.\begin{matrix}H \\ H\end{matrix}\right\} O = C_2H_4O$$

Succinic acid. Succinic anhydride.

$$\left.\begin{matrix}(C_4H_4O_2)'' \\ H_2\end{matrix}\right\} O_2 - \left.\begin{matrix}H \\ H\end{matrix}\right\} O = C_4H_4O_3$$

752. Oxide of ethylene is transformed into vinic alcohol by adding to an aqueous solution of the oxide some sodium amalgam, and surrounding the solution with a freezing mixture, so as to moderate the action; on submitting the solution to distillation, the alcohol distils over; the hydrogen has, therefore, combined directly with the oxide, thus:—

$$C_2H_4O + H_2 = \left.\begin{matrix}C_2H_5 \\ H\end{matrix}\right\} O$$

753. When the oxide of ethylene is mixed in equivalent quantities with bromine, a crystalline mass is obtained; the crystals are insoluble in water, but dissolve in alcohol and ether; they constitute a combination of the oxide with bromine: the formula of the body is $\left.\begin{matrix}C_2H_4O \\ C_2H_4O\end{matrix}\right\} Br_2$; so that the oxide has doubled at the moment of combination. When this bromine compound is heated with sulphuretted hydrogen, or with some of the metals—mercury, for instance—the bromine is removed, and a volatile liquid

is obtained, the empirical formula of which is $C_4H_8O_2$; the rational formula is probably $\left.\begin{matrix}(C_2H_4)''\\(C_2H_4)''\end{matrix}\right\}O_2$.

754. Oxide of ethylene also combines directly with ammonia, forming with that body a series of bases.

755. *Substitution of oxygen for some of the hydrogen in the radicals of the biatomic alcohols.*—These alcohols are unaltered in the air; but mixed with platinum black they attract oxygen with such rapidity that the platinum becomes incandescent. By regulating the conditions of the experiment, however, so as to produce a slow action, aqueous solutions of these alcohols are slowly converted into acids, having the general formula $\left.\begin{matrix}(C_nH_{2n-2}O)''\\H_2\end{matrix}\right\}O_2$. Nitric acid converts ethyl-glycol into glycolic and oxalic acids; the other alcohols ought to yield, by the same treatment, acids corresponding to oxalic acid; the general formula of these acids would be $\left.\begin{matrix}(C_nH_{2n-4}O_2)''\\H_2\end{matrix}\right\}O_2$.

756. The composition of the two series of acids which the following glycols furnish, we here give:—

Glycol.	Propylo-glycol.	Butylo-glycol.
$\left.\begin{matrix}(C_2H_4)''\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}(C_3H_6)''\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}(C_4H_8)''\\H_2\end{matrix}\right\}O_2$
Glycolic acid.	Lactic acid.	Butylo-lactic acid.
$\left.\begin{matrix}(C_2H_2O)''\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}(C_3H_4O)''\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}(C_4H_6O)''\\H_2\end{matrix}\right\}O_2$
Oxalic acid.	Malonic acid.	Succinic acid.
$\left.\begin{matrix}(C_2O_2)''\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}(C_3H_2O_2)''\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}(C_4H_4O_2)''\\H_2\end{matrix}\right\}O_2$

Glycolic acid is also formed when a hydrated salt of chloracetic acid is decomposed by heat, thus:—

$$\left.\begin{matrix}C_2H_2ClO\\M\end{matrix}\right\}O+2HO=MCl+\left.\begin{matrix}(C_2H_2O)''\\H_2\end{matrix}\right\}O_2$$

757. The student will find, when he comes to study the destructive oxidation of organic bodies, that oxalic acid is one of the most frequent products; it is in this way that oxalic acid is manufactured. Starch, sugar, and other like bodies, are oxidized by nitric acid, oxalic acid being the

chief product of that oxidation; but the formation of oxalic acid by this method is totally different from its formation from glycol; in the first case, its formation is attended with the total destruction of the primitive organic substance; but in the case of its formation from glycol, the molecule is modified by the substitution of oxygen for a part of the hydrogen, but the molecule is not destroyed. The oxalic acid stands in the same relation to glycol as acetic acid does to vinic alcohol.

758. Malonic acid has been obtained by the oxidation of malic acid by bichromate of potash; it has not yet been obtained by the oxidation of lactic acid; but there can be no doubt, that by acting upon lactic acid in a proper manner, that acid will yield either malonic acid or an isomeric acid.

759. Succinic acid is obtained from amber; it has also been obtained from malic and tartaric acids: it has not yet been obtained from butylactic acid; but there can be no doubt, by using suitable reagents for the replacement of one atom of oxygen for two atoms of hydrogen in the biatomic molecule in that acid, that succinic or an isomeric acid would be obtained.

760. In addition to the two series of acids we have noticed, two other bodies belonging to the glycol series have been obtained, namely, glyoxal and glyoxylic acid; it is yet doubtful whether glyoxal has been obtained directly from glycol, but glyoxylic acid is found among the products produced by the oxidation of glycol by nitric acid; both were obtained by Debus by acting upon vinic alcohol with nitric acid. Glyoxal possesses all the properties of an aldehyde; it reduces silver salts, and forms crystalline compounds with alkaline bisulphites; its formula is $C_2H_2O_2$; it is, probably, the aldehyde of oxalic acid. Glyoxylic acid is an intermediate compound between glycolic and oxalic acids, just as oil of bitter almonds is intermediate between benzylic alcohol and benzoic acid.

Benzylic alcohol.	**Glycolic acid.**
C_7H_8O.	$C_2H_4O_3$.
Oil of bitter almonds,	**Glyoxylic acid.**
C_7H_6O.	$C_2H_2O_3$.
Benzoic acid.	**Oxalic acid.**
$C_7H_6O_2$.	$C_2H_2O_4$.

And as solution of potash decomposes oil of bitter almonds, and produces benzylic alcohol and benzoate of potash, so the same alkali with glyoxylic acid forms glycolate and oxalate of potash, thus:—

$$2\,C_7H_6O + H_2O = \overset{\text{Benzylic alcohol.}}{C_7H_8O} + \overset{\text{Benzoic acid.}}{C_7H_6O_2}.$$

$$2\,C_2H_2O_3 + H_2O = \overset{\text{Glycolic acid.}}{C_2H_4O_3} + \overset{\text{Oxalic acid.}}{C_2H_2O_4}.$$

In each case, of course, the acid which is formed combines with the potash. And as oil of bitter almonds oxidizes with great ease, and yields benzoic acid, so glyoxylic acid takes up oxygen readily, and becomes converted into oxalic acid.

$$C_7H_6O + O = \overset{\text{Benzoic acid.}}{C_7H_6O_2}$$

$$\overset{\text{Glyoxylic acid.}}{C_2H_2O_3} + O = \overset{\text{Oxalic acid.}}{C_2H_2O_4}$$

761. Debus, who pointed out the relations of glyoxylic acid, has also directed attention to the relations of glyoxal. He regards glyoxal as the aldehyde of oxalic acid; he considers there exists between glycol, glyoxal, and oxalic acid, the same relations which exist between vinic alcohol, aldehyde, and acetic acid.

Vinic alcohol.	Aldehyde.	Acetic acid.
C_2H_6O	C_2H_4O	C_2H_4O
Glycol.	Glyoxal.	Oxalic acid.
$C_2H_6O_2$	$C_2H_2O_2$	$C_2H_2O_4$

762. *Conversion of these biatomic into monatomic alcohols.*—Propyl-glycol heated some hours in a salt-water bath with an excess of concentrated hydriodic acid, is coloured strongly from liberated iodine; on saturating by potash and distilling, we obtain water and an etherial liquid, which is more dense; dehydrated by chloride of calcium, the product boils at 93° C.; its density is 1·725 at 0° C.: its composition is that of iodide of propyle, C_3H_7I.

The two phases of the reaction can be represented by the following equations:—

Propylic glycol. Propylic alcohol.

$$\left.\begin{matrix}(C_3H_6)''\\ H_2\end{matrix}\right\}O_2 + 2HI = \left.\begin{matrix}C_3H_7\\ H\end{matrix}\right\}O + \left.\begin{matrix}H\\ H\end{matrix}\right\}O + II$$

$$\left.\begin{matrix}C_3H_7\\ H\end{matrix}\right\}O + HI = C_3H_7I + \left.\begin{matrix}H\\ H\end{matrix}\right\}O$$

763. Butyl-glycol, treated with hydriodic acid, comports itself in an analogous manner; but glycol is not reduced by the hydriodic acid; for Maxwell Simpson has proved that glycol, under the influence of this acid, is converted into iodide of ethylene.

764. Glycol has been transformed into vinic alcohol in the following way:—Chlorhydrine of glycol, dissolved in half its volume of water, and submitted to the action of sodium amalgam, is converted, at the ordinary temperature, into vinic alcohol.

765. *Action of fused potash on the glycols.*—When ethyle-glycol is fused with hydrate of potash, a large quantity of hydrogen gas is disengaged, and the residue consists principally of oxalate of potash. Alcohol, under similar treatment, yields, as the student will remember, hydrogen and acetate of potash.

(4.) APPENDIX D.

APPENDIX TO THE GLYCOLS.—POLYETHYLENIC BODIES.

766. We have stated that acetic acid and acetic anhydride combine with oxide of ethylene, forming diacetate of glycol. When the diacetate is separated by distillation, there still remains a notable quantity of liquid, the boiling point of which is above 200° C. This liquid can be separated into three products, which we can consider as basic acetates of oxide of ethylene, and which may be considered as constituting acetates of polyethylenic alcohols.

767. The first product boils about 200° C., and constitutes acetate of diethylene, $\left.\begin{matrix}(C_2H_4)''\\ (C_2H_4)''\\ (C_2H_3O)_2\end{matrix}\right\}O_3$. This body, we have also seen, can be formed by adding oxide of ethylene to diacetate of glycol. Saponified by baryta, this

acetate is resolved into acetic acid and diethylenic alcohol, $\left.\begin{matrix}(C_2H_4)_2''\\ H_2\end{matrix}\right\} O_3$.*

768. The second product boils about 290° C., and it constitutes acetate of triethylene, $\left.\begin{matrix}(C_2H_4)_3''\\ (C_2H_3O)_2\end{matrix}\right\} O_4$. Under the influence of baryta, it gives acetate of baryta and triethylenic alcohol, $\left.\begin{matrix}(C_2H_4)_3''\\ H_2\end{matrix}\right\} O_4$.

769. The third product boils about 300° C.; it constitutes acetate of tetrethylene, $\left.\begin{matrix}(C_2H_4)_4''\\ (C_2H_3O)_2\end{matrix}\right\} O_5$. The action of baryta gives acetate of baryta and tetrethylenic alcohol, $\left.\begin{matrix}(C_2H_4)_4''\\ H_2\end{matrix}\right\} O_5$.

770. When glycol is heated with bibromide of ethylene between 110° C. and 120° C., we obtain diethylenic alcohol, water, and bromhydrine of glycol; but along with these there are obtained four other polyethylenic alcohols, viz., triethylenic, tetrethylenic, pentethylenic, $\left.\begin{matrix}(C_2H_4)_5'')\\ H_2\end{matrix}\right\} O_6$, and hexethylenic alcohol, $\left.\begin{matrix}(C_2H_4)_6''\\ H_2\end{matrix}\right\} O_7$.

771. Wurtz and Lourenço, who discovered these bodies, regarded them at first as bodies intermediate between the biatomic alcohols and their ethers. They compared them to the following sulphuric and lactic acid compounds:—

Lactic acid.	Glycol.	Monhydrated sulphuric acid.
$\left.\begin{matrix}(C_3H_4O)''\\ H_2\end{matrix}\right\} O_2$	$\left.\begin{matrix}(C_2H_4)''\\ H_2\end{matrix}\right\} O_2$	$\left.\begin{matrix}SO_2\\ H_2\end{matrix}\right\} O_2$
Pelouzes anhydride of lactic acid.	Diethlylenic body.	Nordhausen sulphuric acid.
$\left.\begin{matrix}(C_3H_4O)''\\ (C_3H_4O)''\\ H_2\end{matrix}\right\} O_3$	$\left.\begin{matrix}(C_2H_4)''\\ (C_2H_4)''\\ H_2\end{matrix}\right\} O_3$	$\left.\begin{matrix}SO_2\\ SO_2\\ H_2\end{matrix}\right\} O_3$
Lactide.	Oxide of ethylene.	Sulphuric anhydride.
C_3H_4O,O	C_2H_4O	SO_3

---

* A diethylenic body has been obtained, in which one atom of ethylene is replaced by succinyl, $\left.\begin{matrix}(C_2H_4)''\\ (C_4H_4O_2)''\\ H_2\end{matrix}\right\} O_3$. It is obtained by adding together succinic acid and glycol, and heating the mixture: it evidently corresponds to the sulphovinic acids.

772. With the progress of their researches, these chemists appear to regard these diethylenic bodies as polyethylenic alcohols. If they are alcohols, then our definition of the term alcohol must be altered; for we have said that alcoholic bodies are constructed on the type of water, in which one half the hydrogen is replaced by a carbohydrogen.

773. If the polyethylenic bodies are alcohols, then it is probable that the body obtained on removing the bromine from oxide of ethylene (753) is the ether of diethylenic alcohol.

774. Wurtz thinks that the polyethylenic bodies may be viewed as the alcohols of diatomic acids. The following facts, which he has discovered, appear to confirm this view.

775. Glycolic, lactic, and oxalic acids, which are derived from the glycols, as we have already seen, by analogous reactions to those which transform vinic alcohol into acetic acid, are simple acids. But this is not the case with the acids Wurtz has obtained by the oxidation of these polyethylenic bodies. There is obtained by the oxidation of diethylenic alcohol, an acid isomeric with malic acid; and under the same circumstances, triethylenic alcohol is transformed into a still more complex acid.

EXERCISE.

153. Write out the formula, and state how you would prepare, the following compounds:—Monosodium butyl-glycol, monethyl propyl-glycol, chlorhydrine of amyl-glycol, dibutyrate of glycol, monacetate of propyl-glycol, distearate of glycol, dibenzoate of amyl-glycol, butyroacetate of glycol, bromhydrate of propyl-glycol.

776. In the appendix to this group the student will learn that when the aldehydes are treated with pentachloride of phosphorus, bichlorides of apparently diatomic radicals are obtained; these diatomic radicals are isomers of the radicals in the biatomic alcohols. When their chlorides are treated with a salt of silver, a combination of the acid of the silver salt and the diatomic radical takes place, corresponding to the compounds obtained on treating the chlorides or bromides of the radicals of the diatomic alcohols with silver salts; but the behaviour of aldehyde compounds with potash is totally different

to the behaviour of the analogous compounds of the glycol group with that reagent; for example, when mono or diacetate of glycol is treated with potash, it is decomposed into the diatomic alcohol, and acetate of potash is formed; but if acetate of aldehyde, $\left.\begin{matrix}(C_2H_4)''\\(C_2H_3O)_2\end{matrix}\right\}O_2$, which is isomeric with diacetate of glycol, be treated with potash, it is decomposed, not into an alcohol, but back again into the aldehyde out of which it sprung, and acetate of potash is formed.

777. Oil of bitter almonds yields, when treated with pentachloride of phosphorus, chlorobenzole $(C_7H_6)''Cl_2$, and if this body be treated with acetate of silver, acetate of benzole, $\left.\begin{matrix}(C_7H_6)''\\(C_2H_3O)_2\end{matrix}\right\}O_2$, is obtained. When this compound was first formed, it was thought to be the acetate of the biatomic alcohol of the benzoic group; but when treated with potash, it is decomposed into oil of bitter almonds and acetic acid; no trace of an alcohol of this formula, $\left.\begin{matrix}(C_7H_6)''\\H_2\end{matrix}\right\}O_2$, could be obtained.

(5.) APPENDIX E.

THE BIATOMIC ALCOHOL GROUP.

778. When the aldehydes are acted upon by pentachloride or pentabromide of phosphorus, compounds are formed containing biatomic radicals, not identical, but *isomeric* with the biatomic radicals forming the olefiant gas series. We have now to learn that from the aldehydes a series of bodies can be prepared isomeric with the glycol compounds; they would appear, from their composition, to be derived from biatomic alcohols; the aldehydes, as regards these compounds, would, therefore, be viewed as the oxides or ethers of these alcohols; the formula of the alcohol of aldehyde would be $\left.\begin{matrix}(C_2H_4)''\\H_2\end{matrix}\right\}O_2$.

779. *Combination of aldehyde with electro-negative radicals.*—Dry hydrochloric acid gas passed to saturation

into aldehyde, kept cool by a freezing mixture, converts it into a body called oxychloride of ethylidene, which may be regarded as a double molecule of aldehyde, in which one atom of O is replaced by two atoms of Cl; the formula of this body is, therefore, $\left.\begin{matrix}(C_2H_4)''\\(C_2H_4)''\end{matrix}\right\}\begin{matrix}O\\Cl_2\end{matrix}$.

780. When equivalent weights of aldehyde and acetic anhydride are heated together in a sealed tube to 180°C. for twelve hours they combine, biacetate of aldehyde being formed, $\left.\begin{matrix}(C_2H_4)''\\(C_2H_3O)\\(C_2H_3O)\end{matrix}\right\}O_2$; this body is metameric with biacetate of ethylene. If aldehyde and chloride of acetyle be heated together to 100°C. in a sealed tube for three hours, they combine in the proportion of single equivalents of each of the two substances.

781. *Combination of aldehyde with electro-positive radicals.*—When bromide of ethylidene is made to act on ethylate of sodium, bromide of sodium and acetal is formed, thus:—

$$(C_2H_4)''Br_2 + 2\left(\left.\begin{matrix}C_2H_5\\Na\end{matrix}\right\}O\right) = 2\,NaBr + \left.\begin{matrix}(C_2H_4)''\\(C_2H_5)_2\end{matrix}\right\}O_2$$

Acetal, which is also formed by the oxidation of vinic alcohol, is isomeric with diethyl-glycol.

782. If a mixture of sulphuric acid, water, peroxide of manganese, and ethylic and methylic alcohols be distilled, the two following compounds are obtained:—

$$\text{(1.)}\quad \left.\begin{matrix}(C_2H_4)''\\(CH_3)_2\end{matrix}\right\}O_2 \qquad\Big|\qquad \text{(2.)}\quad \left.\begin{matrix}(C_2H_4)''\\(CH_3)\\(C_2H_5)\end{matrix}\right\}O_2$$

They are, in fact, acetals, in which one or both atoms of ethyl have been replaced by methyl.

783. When chlorine acts on ethylic alcohol, the following substances are obtained:—

$$C_6H_{13}ClO_2 = \left.\begin{matrix}(C_2H_3Cl)''\\(C_2H_5)_2\end{matrix}\right\}O_2\text{, monochlorinated acetal.}$$

$$C_6H_{12}Cl_2O_2 = \left.\begin{matrix}(C_2H_2Cl_2)''\\(C_2H_5)_2\end{matrix}\right\}O_2\text{, bichlorinated acetal.}$$

$$C_6H_{11}Cl_3O_2 = \left.\begin{matrix}(C_2HCl_3)''\\(C_2H_5)_2\end{matrix}\right\}O_2\text{ trichlorinated acetal.}$$

784. When perfectly dry chlorine is passed into anhydrous alcohol to saturation, a body termed chloral is produced : its formula is $C_2 H Cl_3 O$; it therefore stands to trichlorinated acetal as aldehyde does to acetal.

785. The other aldehydes form compounds similar to those which we have seen the acetic aldehyde forms. The aldehyde of valerianic acid has been combined with acetic and benzoic acids.

$$\left.\begin{matrix}\text{Acetic}\\ \text{compound}\end{matrix}\right\} \left.\begin{matrix}(C_5 H_{10})''\\ (C_2 H_3 O)_2\end{matrix}\right\} O_2 \quad \Bigg| \quad \left.\begin{matrix}\text{Benzoic}\\ \text{compound}\end{matrix}\right\} \left.\begin{matrix}(C_5 H_{10})''\\ (C_7 H_5 O)_2\end{matrix}\right\} O_2$$

These compounds are respectively decomposed by caustic potash into valerianic aldehyde, and acetate and benzoate of potash. Acetate of valerianic aldehyde is isomeric with diacetate of amylo-glycol.

NEGATIVE GROUP.

786. This group embraces—(1) Mineral biatomic acids. (2) Organic biatomic acids. (3) Salts of the bibasic acids. (4) Ethers of the bibasic acids.

BIATOMIC ACIDS.

787. The substitution of a biatomic acid radical for two atoms of hydrogen in two molecules of water, produces a biatomic acid.

788. The bibasic acids give neutral salts and acid salts. Neutral salts are produced when both atoms of the basic hydrogen are exchanged for a metal; acid salts when only one atom of the basic hydrogen is replaced by a metal. Examples :—

Bisulphate of potassium.	Sulphate of potassium.
$\left.\begin{matrix}(S O_2)''\\ H K\end{matrix}\right\} O_2$	$\left.\begin{matrix}(S O_2)\\ K_2\end{matrix}\right\} O_2$

789. The acid salts are frequently produced by double decomposition ; they are generally very stable.

790. The bibasic acids can produce, with each alcohol, two ether salts—a neutral ether salt, and an acid ether salt. *Considered in a state of vapour under the same volume, the neutral ethers of the bibasic acids contain twice*

the amount of the alcohol radical which the neutral ethers of the monobasic acids contain.

791. ***Considered in the state of vapour under the same volume, the chlorides of the bibasic acids contain twice the amount of chlorine that the monobasic acids contain.***

792. The ammoniacal salts of the bibasic acids are not volatile without decomposition; frequently they give by heat the primary diamides, the secondary amides (imides), or the acid amides.

793. The anhydrides of the biatomic acids are produced by *dehydration*, whereas the monatomic anhydrides are produced by the *substitution* of an acid radical for the typical hydrogen in the acid. According to the old theory, both groups of acids contain water, and therefore, in accordance with that theory, the anhydrides of the monatomic acids ought to be procured by dehydration as well as the anhydrides of the biatomic acids. But when we view them according to the type theory, we can account for the necessity of forming the monatomic anhydrides by substitution, because these acids do not contain the elements of water; but the biatomic acids do contain, according to this theory, the elements of water; and therefore their anhydrides can be procured by dehydrating the acids: thus, $\left.\begin{matrix}(SO_2)''\\H_2\end{matrix}\right\}O_2$ is the formula of sulphuric acid, on the type-theory. When it is dehydrated we obtain SO_3, or SO_2O, which is sulphuric anhydride. We might, therefore, write the formula of sulphuric acid, and all other biatomic acids, in a somewhat different manner, so as to indicate their separation into water, and the anhydrides, thus: H_2O, SO_3. Many of the biatomic acids are transformed into their anhydrides by the action of heat, or dehydrating agents, such as phosphoric anhydride.

(1.) Mineral Acids.

794. The following are the principal bibasic inorganic acids:—

Carbonic acid (hypothetical)	$\left.\begin{matrix}(CO)''\\H_2\end{matrix}\right\}O_2$	Carbonic anhydride	CO_2
Sulphurous acid (hypothetical)	$\left.\begin{matrix}(SO)''\\H_2\end{matrix}\right\}O_2$	Sulphurous anhydride	SO_2

Sulphuric acid $\left.\begin{matrix}(SO_2)'\\H_2\end{matrix}\right\}O_2$ Sulphuric anhydride SO_3

Chromic acid $\left.\begin{matrix}(Cr_2O_2)''\\H_2\end{matrix}\right\}O_2$ Chromic anhydride Cr_2O_3

(2.) BIATOMIC ORGANIC ACIDS.

795. Generally the bibasic acids are not volatile without decomposition; sometimes they are transformed by heat into their anhydrides.

796. The bibasic organic acids submitted to the action of chlorine, of bromine, or of nitric acid, form the conjugated derivatives less easily than the monobasic acids. They form sometimes conjugated acids with sulphuric acid, which are tribasic. For example, sulphosuccinic acid.

FIRST CLASS.

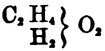
(*General formula*, $\left.\begin{matrix}C_nH_{2n-2}O\\H_2\end{matrix}\right\}O_2$.)

797. Several memoirs have been written both by Kolbe and Wurtz upon the basicity of lactic acid, one of the acids belonging to this group. Kolbe maintains that it is monobasic; Wurtz maintains that it is *biatomic*, and in some points of view it is *bibasic*. The reasons Kolbe assigns for regarding it as monobasic we cannot now enter upon, as they are connected with that chemist's views as regards the constitution of chemical compounds in general, but the student will find the memoirs of Kolbe and Wurtz in the 1st, 2nd, and 3rd volumes of the "Répertoire de Chimie Pure."

798. Wurtz considers that its biatomic nature is proved—1st, by its formation from propyl-glycol; for, as the oxidation of vinic alcohol, which is monatomic, gives rise to a monatomic acid, the oxidation of a biatomic alcohol must produce a biatomic acid. 2nd. That its biatomic nature is proved, he thinks, by the fact that lactic anhydride is formed from lactic acid by the simple elimination of water, whereas we do not know of any monatomic acid which will yield its anhydride in this way; in fact, as monatomic acids do not contain, *in one equivalent*, the anhydride and the elements of water, it is impossible for their anhydrides to be formed from the acids by the separation of water. Lactic anhydride, like the anhydrides of all biatomic acids, contains the same number of equivalents of carbon and hydrogen as its acid,

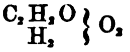
whereas the anhydrides of the monatomic acids contain double the number of equivalents of carbon and hydrogen that their acids contain. The two atoms of typical hydrogen in lactic acid which it must contain if it is diatomic, cannot be replaced as they can in bibasic acids, like oxalic acid, by two atoms of an *alkaline metal;* only one atom of hydrogen in lactic acid can be replaced by an atom of potassium; and further, this potassium salt is neutral, whilst the potassium salt of oxalic acid which contains only one atom of potassium is acid; therefore lactic acid, like monobasic acids, only forms one class of salts with the *alkaline metals,* and the alkaline salts of lactic acid, like the alkaline salts of the monobasic acids, are neutral. Whereas bibasic acids, like oxalic acid, form two classes of salts with the alkaline metals; one class containing one atom of the metal in place of one of the hydrogen atoms; these salts are acid. Example:—Acid oxalate of potash, $\left.\begin{matrix}C_2O_2\\KH\end{matrix}\right\}O_2$. In the other class both atoms of the hydrogen are replaced by two atoms of the alkaline metals: these salts are neutral. Example:—Neutral oxalate of potash, $\left.\begin{matrix}C_2O_2\\KK\end{matrix}\right\}O_2$. Although only one atom of hydrogen in lactic acid can be replaced by an atom of an alkaline metal, the two atoms can be replaced by ethyl and by electro-negative metals, such as tin. Wurtz explains these and other apparently contradictory facts, which we shall presently notice, in the following manner. He considers that the typical hydrogen is not always, or necessarily, basic; the more oxygenized the radical the more the typical hydrogen tends to become basic; the hydrogen in oxalic acid is, therefore, more basic than the hydrogen in glycolic acid, although both acids are produced from the same diatomic body, glycol.

Glycol.



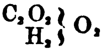
$$\left.\begin{matrix}C_2H_4\\H_2\end{matrix}\right\}O_2$$

Glycolic acid.



$$\left.\begin{matrix}C_2H_2O\\H_2\end{matrix}\right\}O_2$$

Oxalic acid.



$$\left.\begin{matrix}C_2O_2\\H_2\end{matrix}\right\}O_2$$

It is therefore necessary, Wurtz thinks, to establish a difference between the term *diatomic,* which is applied to the complication of the molecule, and the term *bibasic,* which is applied to the capacity of saturation.

799. Chloride of lactyl ($C_3H_4OCl_2$) was obtained by

Wurtz by acting upon lactate of lime with perchloride of phosphorus; from this chloride, lactic acid can be regenerated; and if the chloride be made to act upon ethylate of soda, we obtain lactic di-ether $\left.\begin{matrix}(C_3H_4O)''\\ C_2H_5\\ C_2H_5\end{matrix}\right\}O_2$ which is neutral. If this lactic di-ether be treated with potash, alcohol is set at liberty, and an acid is formed which saturates the potash. This acid, in which one atom of the typical hydrogen in lactic acid has been replaced by ethyl, is called ethyl-lactic acid; its formula is $\left.\begin{matrix}(C_3H_4O)''\\ C_2H_5\\ H\end{matrix}\right\}O_2$; the formula of its potash salt is $\left.\begin{matrix}(C_3H_4O)''\\ C_2H_5\\ K\end{matrix}\right\}O_2$. If we distil a mixture of sulphovinate of potash and lactate of lime, or if we heat in a sealed tube to 170°C. a mixture of lactic acid and alcohol, we obtain an ether which is *neutral*, although only one atom of the typical hydrogen in lactic acid has been replaced by an atom of ethyl; it is called lactate of monethyl ether, and it is only isomeric, not identical with the acid called ethyl-lactic acid. Potassium dissolves in the lactate of monethyl ether, hydrogen is disengaged, and there is formed a compound isomeric not identical with ethyl-lactate of potash. Ethyl-lactic acid and lactate of monethyl ether are most curious examples of isomerism; they are formed by the same acid, they contain the same radical ethyl, and the same amount of it, yet one is an acid, the other is a perfectly neutral body. Wurtz explains this difference by supposing that the two atoms of typical hydrogen in the acid possess different properties,—one atom is strongly basic; it can therefore be replaced by a metal or by an organic group, such as ethyl; and when it is thus replaced, the compound produced is *neutral*. The other atom of hydrogen can be easily replaced by the radicals of acids, or by an indifferent group, such as ethyl, and when it is thus replaced, the compound produced is still an acid, because the basic atom of hydrogen of the lactic acid remains. Wurtz, therefore, draws the distinction between the properties of the two atoms of hydrogen in writing the formulæ of lactic and the other acids of this group. For example, he writes the formula of lactic acid thus: $\left.\begin{matrix}H\\(C_3H_4O)'\\H\end{matrix}\right\}O_2$. We have said that acids can be formed in which the non-basic atom of hydrogen in the lactic acid is replaced by an acid radical; butyro-lactic ether $\left(\left.\begin{matrix}(C_4H_7O)\\(C_3H_4O)'\\(C_2H_5)\end{matrix}\right\}O_2\right)$, for example, is obtained when an alcoholic solution of butyrate of potash is added to chlorolactic ether.

800. Wurtz expresses the relations of these different compounds by the following formulæ:—

Lactic acid.	Lactate of potash.	Lactate of monethyl ether.	Lactate of potassio-ether.	Lactate of diethyl ether.
$\left.\begin{matrix}H\\(C_3H_4O)''\\H\end{matrix}\right\}O_2$	$\left.\begin{matrix}H\\(C_3H_4O)''\\K\end{matrix}\right\}O_2$	$\left.\begin{matrix}H\\(C_3H_4O)''\\(C_2H_5)\end{matrix}\right\}O_2$	$\left.\begin{matrix}K\\(C_3H_4O)''\\(C_2H_5)\end{matrix}\right\}O_2$	$\left.\begin{matrix}(C_2H_5)\\(C_3H_4O)''\\(C_2H_5)\end{matrix}\right\}O_2$
	Butyro-lactic acid.	Ethylo-lactic acid.	Ethylo-lactate of potash.	
	$\left.\begin{matrix}(C_4H_7O)\\(C_3H_4O)''\\H\end{matrix}\right\}O_2$	$\left.\begin{matrix}(C_2H_5)\\(C_3H_4O)''\\H\end{matrix}\right\}O_2$	$\left.\begin{matrix}(C_2H_5)\\(C_3H_4O)''\\K\end{matrix}\right\}O_2$	

801. If we treat lactate of potassio-ether, or ethylo-lactate of potash, with an alcoholic solution of iodide of ethyl, we obtain lactate of di-ethyl ether.

802. We have seen already that many polyatomic radicals are capable of multiplying themselves in compounds, forming bodies on still more condensed types by this multiplication. Lactyl is no exception to this rule. If a mixture of chlorolactic ether and lactate of potash is heated in a sealed tube to 100° C., chloride of potassium and dilactate of monethyl ether, $\left.\begin{matrix}(C_3H_4O)'\\(C_3H_4O)'\\C_2H_5\\H\end{matrix}\right\}O_3$ are formed: the dilactate of di-ethyl ether can also be formed.

These compounds constitute the ethers of Pelouze's anhydride of lactic acid, $\left.\begin{matrix}(C_3H_4O)'\\(C_3H_4O)'\\H_2\end{matrix}\right\}O_3$. Trilactate of Di-ethyl ether, $\left.\begin{matrix}(C_3H_4O)'_3\\(C_2H_5)_2\end{matrix}\right\}O_4$, is obtained by keeping a mixture of lactic anhydride and lactate of diethyl ether in a sealed tube for several days, at a temperature of 140° C.: succinolactic diethyl ether, $\left.\begin{array}{l}(C_4H_4O_2)''\\(C_3H_4O)''\\(C_2H_5)_2\end{array}\right\}O_3$ has also been formed.

803. The following is a list of the acids, as yet known, belonging to this class. The student must commit to memory their names and formulæ:—

Glycolic acid - - - - $\left.\begin{array}{c}H\\(C_2H_2O)\\H\end{array}\right\}O_2$

Lactic acid - - - - - $\left.\begin{array}{c}H\\(C_3H_4O)\\H\end{array}\right\}O_2$

Leucic acid - - - - $\left.\begin{array}{c}H\\(C_6H_{10}O)\\H\end{array}\right\}O_2$*

804. These acids are very soluble in water; they are not volatile without decomposition.

805. *Preparation.*—Sugar of milk yields by fermentation lactic acid; cane sugar can also be made to yield lactic acid, and not alcohol, by fermentation. This acid, we have already seen, is obtained by the oxidation of propyl-glycol. Glycolic acid is produced by the oxidation of vinic alcohol by nitric acid; it is also formed, as we have seen, by the oxidation of ethylo-glycol; it is also formed when a hydrated salt of chloracetate of potash is decomposed by heat. Perkins and Duppa have obtained it on treating bromacetic acid with oxide of silver or potash. They have also obtained glyoxilic acid on treating bibromacetic acid with the same reagents. We give the empirical formulæ of acetic, glycolic, and glyoxilic acids, in order that the student may see how these bodies are related, as regards their composition:—

Acetic acid.	Glycolic acid.	Glyoxilic acid.
$C_2H_4O_2$	$C_2H_4O_3$	$C_2H_4O_4$

806. The acids of this group are also produced by treating certain amides with nitrous acid. Alanine (propionamic acid) yields, as we have seen (490), on being treated with

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* Butyro-lactic acid will belong to this group.

nitrous acid, lactic acid. When gelatine is boiled with a strong solution of one of the alkalies, ammonia is evolved, and a sweet crystallizable substance, called sugar of gelatine, or glycocoll (or better, glycocine), and another crystallizable body, called leucine, are formed. This latter body is also one of the products formed on boiling albumen, fibrine, or caseine, in a strong solution of the alkalies. Glycocine, on being treated with nitrous acid, yields glycolic acid; and leucine, on being treated with the same reagent, yields leucic acid. The three amidic bodies are homologous, as will be seen from the following formulæ:—

Glycocine - - - - -	$C_2H_5NO_2$
Alanine - - - - -	$C_3H_7NO_2$
Leucine - - - - -	$C_6H_{13}NO_2$

807. These acids give, as we have already noticed, conjugated acids, when they are treated with certain monobasic acids. Thus, with benzoic acid, we can obtain benzo-glycolic acid and benzo-lactic acid:—

Benzo-glycolic acid - - -
$$\left.\begin{array}{c}(C_2H_2O)''\\(C_7H_5O)\\H\end{array}\right\}O_2$$

Benzo-lactic acid - - -
$$\left.\begin{array}{c}(C_3H_4O)''\\(C_7H_5O)\\H\end{array}\right\}O_2$$

808. An acid called hippuric acid, which occurs in combination with potash and soda in the urine of horses and cows, and other graminivorous animals, is considered to be the amidogen compound of benzo-glycolic acid, because, when treated with nitrous acid, it undergoes the decomposition peculiar to amidogen compounds, viz., the formation of a non-nitrogenous acid, water, and the liberation of nitrogen. The acid formed on treating hippuric acid with nitrous acid, is benzo-glycolic acid. Under the influence of water, this conjugate acid splits up into benzoic and glycolic acids. Dessaignes has actually succeeded in regenerating hippuric acid by the action of chloride of benzoyl upon the zinc compound of glycocine:—

$$\underset{\text{Zinc compound of glycocine.}}{C_2H_5NO_2Zn} + \underset{\text{Chloride of benzoyl.}}{C_7H_5OCl} = \underset{\text{Hippuric acid.}}{C_9H_9NO_3} + ZnCl + H$$

809. This is not the only view which has been entertained of the constitution of hippuric acid; but it appears, as far as our information at present extends, to be the most probable.

810. Lautermann has lately transformed lactic acid into propionic acid in the following way:—The acid, diluted with an equal volume of water, is saturated with hydriodic acid gas; it is then heated in a sealed tube to 140° C.; the hydriodic acid is decomposed, iodine is liberated, water and propionic acid formed.

SECOND CLASS.

(*General formula,* $\left.\begin{array}{c}C_n H_{2n-4} O_2\\H_2\end{array}\right\} O_2$.)

811. The lowest member of this class of acids, oxalic acid, is obtained by the oxidation of ethyl-glycol. Two other members of the class, pyrotartaric and succinic acids, have been obtained by Simpson by decomposing the cyanides of the biatomic radicals by potash,—cyanide of ethylene yielding succinic, and cyanide of propylene yielding pyrotartaric acids, when treated in this way. This class of acids is, no doubt, the highest of two or more series of acids which the biatomic alcohols of the glycol class yield by oxidation. Some of these alcohols, we have seen, are already known; many remain still unknown.

812. The following is a list of the acids, as yet known, belonging to this class. The student must commit to memory their names and symbols:—

	Fusing point, F.	
Oxalic acid	Sublimes before fusing	$\left.\begin{array}{r}C_2 O_2\\H_2\end{array}\right\} O_2$
Malonic acid	140° F.	$\left.\begin{array}{c}C_3 H_2 O_2\\H_2\end{array}\right\} O_2$
Succinic acid	356	$\left.\begin{array}{c}C_4 H_4 O_2\\H_2\end{array}\right\} O_2$
Pyrotartaric acid	290	$\left.\begin{array}{c}C_5 H_6 O_2\\H_2\end{array}\right\} O_2$*
Adipic acid	266	$\left.\begin{array}{c}C_6 H_8 O_2\\H_2\end{array}\right\} O_2$

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* An acid called lipic acid, found among the products of the oxidation of oils and oily acids, has also had this formula assigned to it.

	Fusing point, F.	
Pimelic acid	257°	$\left.\begin{matrix}C_7H_{10}O_2\\H_2\end{matrix}\right\}O_2$
Suberic acid	257	$\left.\begin{matrix}C_8H_{12}O_2\\H_2\end{matrix}\right\}O_2$
Anchoic acid	237° to 241°	$\left.\begin{matrix}C_9H_{14}O_2\\H_2\end{matrix}\right\}O_2$*
Sebacic acid	260	$\left.\begin{matrix}C_{10}H_{16}O_2\\H_2\end{matrix}\right\}O_2$

813. *Physical properties.*—These acids are solid bodies; they are soluble in water, but their solubility decreases as their atomic weights increase; thus, oxalic acid is very soluble in water, sebacic acid only slightly so; they are soluble in alcohol and ether, and they are easily obtained in the form of crystals. They possess considerable volatility, and may be partially sublimed without undergoing decomposition.

814. *Preparation.*—Pyrotartaric acid is obtained by the destructive distillation of tartaric acid. Suberic acid is a product of the oxidation of cork by nitric acid. Succinic acid is obtained in the distillation of amber: butyric acid has also been transformed into this acid by nitric acid; it can also be obtained, as we shall presently see, by the action of hydriodic acid upon malic and tartaric acids. Suberic and succinic acids have also been formed by the long-continued action of nitric acid upon stearic acid. Malonic acid is obtained by oxidizing malic acid with bichromate of potash. Anchoic acid is found among the products of oxidation of Chinese wax and also of cocoa-nut oil. Sebacic acid is a constant product of the distillation of oleic acid, olein, and all fatty substances containing these bodies. Adipic and pimelic, as well as succinic, suberic, and sebacic acids are obtained by the oxidation of the fatty acids (674); there is, therefore, a close relation between this class of bibasic acids and the monobasic acids of the first class, for the oxidation of the latter gives rise to the formation of the former; this relation is still further proved by the fact that when these bibasic acids are decomposed by heat, carbonic acid and an acid belonging to the acetic series are generally found amongst

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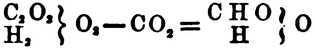
* Called by Wurtz, lepargylic acid.

the products. This is what might naturally be expected, for it will be seen, on comparing corresponding members of the two series of acids, that these bibasic acids contain in one equivalent, an equivalent of a monobasic acid and an equivalent of carbonic acid; thus, if we subtract from oxalic acid an equivalent of carbonic acid, we have left the elements, and in their proper proportions, to form formic acid.



$$\left.\begin{matrix}C_2O_2\\H_2\end{matrix}\right\}O_2-CO_2=\left.\begin{matrix}CHO\\H\end{matrix}\right\}O$$

We might, therefore, suppose that these bibasic acids are formed by the union of carbonic acid with the monobasic acids.

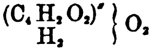
815. It will be seen by the following table, that if two equivalents of oxygen are substituted in a monobasic acid for two equivalents of hydrogen, a corresponding bibasic acid must be produced:—

Acids.			Acids.
Acetic -	$= C_2H_4O_2$	$C_2H_2O_4$	= Oxalic
Propionic -	$= C_3H_6O_2$	$C_3H_4O_4$	= Malonic
Butyric -	$= C_4H_8O_2$	$C_4H_6O_4$	= Succinic
Valeric -	$= C_5H_{10}O_2$	$C_5H_8O_4$	= Pyrotartaric
Caproic -	$= C_6H_{12}O_2$	$C_6H_{10}O_4$	= Adipic
Œnanthylic	$= C_7H_{14}O_2$	$C_7H_{12}O_4$	= Pimelic
Caprylic -	$= C_8H_{16}O_2$	$C_8H_{14}O_4$	= Suberic
Pelargonic -	$= C_9H_{18}O_2$	$C_9H_{16}O_4$	= Anchoic
Rutic -	$= C_{10}H_{20}O_2$	$C_{10}H_{18}O_4$	= Sebacic

THIRD CLASS.

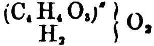
816. In this group is a list of still unclassified bibasic acids; the most important are malic acid and tartaric acid: the student must commit to memory their names and symbols.

Fumaric acid - - - -



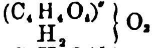
$$\left.\begin{matrix}(C_4H_2O_2)''\\H_2\end{matrix}\right\}O_2$$

Malic acid - - - -



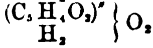
$$\left.\begin{matrix}(C_4H_4O_3)''\\H_2\end{matrix}\right\}O_2$$

Tartaric acid - - - -



$$\left.\begin{matrix}(C_4H_4O_4)''\\H_2\end{matrix}\right\}O_2$$

Pyrocitric acid - - -



$$\left.\begin{matrix}(C_5H_4O_2)''\\H_2\end{matrix}\right\}O_2$$

Mucic acid . . . . . $\left.\begin{matrix}(C_6H_8O_6)''\\H_2\end{matrix}\right\}O_2$

Camphoric acid . . . . $\left.\begin{matrix}(C_{10}H_{14}O_2)''\\H_2\end{matrix}\right\}O_2$

817. Malic and tartaric acids have both been prepared artificially from succinic acid, and they have both been decomposed into that acid.

818. Malic acid is the acid of apples, pears, and various other fruits; in gooseberries, currants, &c., it is associated with citric acid. It has been prepared from bromo-succinic acid, by submitting that acid to the action of oxide of silver, thus:—

$$2\left(\left.\begin{matrix}(C_4H_3BrO_2)''\\H_2\end{matrix}\right\}O_2\right)+\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O+\left.\begin{matrix}H\\H\end{matrix}\right\}O=2\left(\left.\begin{matrix}(C_4H_4O_3)''\\H_2\end{matrix}\right\}O_2\right)+2AgBr.$$

It has also been converted into succinic acid by digesting it in sealed tubes with hydriodic acid, thus:—

$$\left.\begin{matrix}(C_4H_4O_3)''\\H_2\end{matrix}\right\}O_2+2HI=\left.\begin{matrix}(C_4H_4O_2)''\\H_2\end{matrix}\right\}O_2+\left.\begin{matrix}H\\H\end{matrix}\right\}O+II$$

When in the presence of fermenting substances, especially putrefying casein, it is decomposed into succinic, acetic, and carbonic acids.

819. Asparagin and aspartic acid appear to stand in the same relation to malic acid as oxamide and oxamic acid stand to oxalic acid.

820, Tartaric acid is the acid of grapes, of tamarinds, of the pine-apple, and various other fruits, in which it occurs in the state of an acid potash-salt. Liebig has found that this acid is produced by the action of nitric acid upon milk sugar. It has also been obtained from succinic acid by digesting bibromo-succinic acid upon oxide of silver, thus:—

$$\left.\begin{matrix}(C_4H_2Br_2O_2)''\\H_2\end{matrix}\right\}O_2+\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O+\left.\begin{matrix}H\\H\end{matrix}\right\}O=\left.\begin{matrix}C_4H_4O_4\\H_2\end{matrix}\right\}O_2+2AgBr.$$

When it is submitted in sealed tubes to the action of hydriodic acid, it is converted into succinic acid, thus:—

$$\left.\begin{matrix}(C_4H_4O_4)''\\H_2\end{matrix}\right\}O_2+4HI=\left.\begin{matrix}(C_4H_4O_2)\\H_2\end{matrix}\right\}O_2+2H_2O+4I$$

Fourth Class.

(*General formula,* $\left.\begin{array}{c}C_nH_{2n-12}O_2\\H_2\end{array}\right\}O_2$.)

821. Only two acids belonging to this group are known—

Phthalic acid - - - - $\left.\begin{array}{c}(C_8H_4O_2)''\\H_2\end{array}\right\}O_2$

Terephthalic acid - - - $\left.\begin{array}{c}(C_8H_4O_2)''\\H_2\end{array}\right\}O_2$

822. Phthalic acid is obtained by the action of nitric acid on bichloride of naphthalin. Terephthalic acid (insolinic acid) was first obtained by Caillot; he obtained it by acting upon oil turpentine with nitric acid, and he named it terephthalic acid on account of its generation from turpentine, and its *isomerism* with phthalic acid. Hofmann subsequently obtained an acid by acting on cuminic acid with chromic acid; he called this acid insolinic acid; he gave it the formula $\left.\begin{array}{c}(C_9H_6O_2)''\\H_2\end{array}\right\}O_2$. Warren de la Rue and Müller have recently obtained terephthalic acid by acting upon certain liquid hydrocarbons in Rangoon tar with nitric acid. These chemists have found that *insolinic acid* is *only* terephthalic acid.* For the peculiarities of this bibasic acid, we must refer the student to the two last-named chemists' paper on this acid in the "Proc. Royal Soc.," vol. xi., p. 112.

(3.) Salts of the Bibasic Acids.

823. Bibasic acids, as we have already stated, form two classes of salts, acid salts and neutral salts. The acid salts are termed the primary salts; the neutral salts are termed the secondary salts. Example:—

Primary oxalate of potassium. (Acid oxalate of potassium.)	Secondary oxalate of potassium. (Neutral oxalate of potassium.)
$\left.\begin{array}{c}(C_2O_2)''\\HK\end{array}\right\}O_2$	$\left.\begin{array}{c}(C_2O_2)''\\K_2\end{array}\right\}O_2$

824. We have seen (688) that in some of the monatomic organic acids, some of the hydrogen in the acid radical can be replaced by SO_2, and that these sulpho-

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* The student must correct the formula at par. 692.

acids are bibasic. In the following exercises the salts of these sulpho-acids will be introduced, as well as the salts of the bibasic organic and inorganic acids.

EXERCISES.

154. Write out the formulæ of the following salts:—Primary carbonate of potassium, secondary sulphite of sodium, primary sulphate of ammonium, secondary oxalate of potassium, tartrate of potassium and sodium, primary sulpho-benzoate of sodium, acid succinate of sodium, neutral malate of zinc, terephthalate of silver, neutral suberate of lead, primary sulphacetate of sodium, benzo-glycolate of ammonium, neutral sebate of lime.

155. There is a basic sulphate of copper having this composition (employing the old atomic numbers), $4\,Cu\,O, S\,O_3$: formulate it on the water type, employing the new atomic numbers.

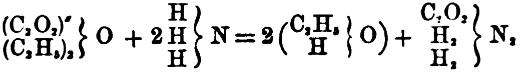
(4.) BIATOMIC ETHERS.

825. The *neutral* biatomic ethers are produced in the same way as the monatomic ethers. When the corresponding acid is not volatile, the neutral ether of the acids is not volatile. In this case we cannot employ distillation as a mode of preparing them, but we operate thus;—hydrochloric acid gas is passed into the solution of the organic acid in alcohol; we neutralize the acid liquid with a carbonate, and we repeatedly agitate with ordinary ether: the ether salt is dissolved by the ether, and is left as a residue on the evaporation of the latter. These neutral ethers can contain two different alcohol radicals. They are obtained by the distillation of two vinic salts, thus:—

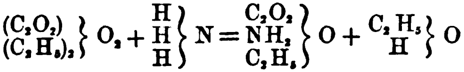
$$\left.\begin{matrix} C_2O_2 \\ (C_2H_5)K \end{matrix}\right\} O_2 + \left.\begin{matrix} S\,O_2 \\ (C\,H_3)K \end{matrix}\right\} O_2 = \left.\begin{matrix} (C_2O_2)'' \\ (C_2H_5) \\ (C\,H_3) \end{matrix}\right\} O_2 + \left.\begin{matrix} (S\,O_2)'' \\ K \end{matrix}\right\} O_2$$

826. In contact with water, but especially with caustic potash, the neutral ethers are decomposed either into alcohol and a vinic salt, or into alcohol and a metallic salt of the corresponding acid.

827. Ammonia transforms the neutral ethers either into an alcohol and a diamide, or into an alcohol and ether of the acid amide, thus:—

(1.)


$$\left.\begin{matrix}(C_2O_2)''\\(C_2H_5)_2\end{matrix}\right\}O+2\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N=2\left(\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O\right)+\left.\begin{matrix}C_2O_2\\H_2\\H_2\end{matrix}\right\}N_2$$

(2.)


$$\left.\begin{matrix}(C_2O_2)\\(C_2H_5)_2\end{matrix}\right\}O_2+\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N=\left.\begin{matrix}C_2O_2\\NH_2\\C_2H_5\end{matrix}\right\}O+\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$$

828. The acid ethers are produced when we heat an alcohol with the bibasic acids. In the free state these acid ethers are generally unstable, and are decomposed promptly by ebullition with water, or with an alkali, into alcohol and the corresponding acid. Generally they are not volatile without decomposition. They form monobasic salts, ordinarily more stable than themselves. These salts can be employed, as we have seen, in double decompositions, for transporting the alcohol radicals into other combinations. They are analogous, as regards composition and acidity, to the primary salts of the bibasic acids; but the acids in these acid ethers do not give their usual reactions with reagents. Thus, in the sulphovinates, the sulphuric acid is not precipitated by salts of baryta in the same manner as it is from metallic sulphates; but a prolonged contact of these ethers with water decomposes them; the sulphuric acid can then be detected. This non-precipitation of sulphuric acid by baryta is not limited, however, to the acid ethers; in some, at least, of the neutral ethers it is not precipitated.

829. We shall now give a course of exercises, in which the student will have to write out the formulæ of the neutral ethers of the bibasic acids, and also the salts formed by inorganic bases with the acid ethers.

EXERCISE.

156. Write out the formulæ for—Primary carbonic ethyl-ether (carbovinic acid), secondary carbonic ethyl-ether (carbonate of ethyl), primary sulphuric amyl-ether (sulphamylic acid), carbovinate of potassium, secondary sulphuric methyl-ether, sulpho-methylate of calcium, oxalovinic acid, tartro-methylate of barium, sebate of ethyl, suberate of methyl, pimelate of amyl, fumarate of ethyl, malovinate of barium, succinate of methyl.

TREBLE MOLECULE.

$$\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3$$

POSITIVE GROUP.

830. This group embraces—(1) The metallic derivatives of water. (2) The triatomic alcohols.

(1.) HYDRATES OF THE METALS PROPER (PRIMARY DERIVATIVES). ANHYDROUS OXIDES (SECONDARY DERIVATIVES).

831. *Primary derivatives.*—The sesqui-atomic and triatomic metals, given under the treble molecule of hydrogen (H_3 H_3), form hydrates on the type of a treble molecule of water; the general formula of these hydrates is, therefore, $\left.\begin{matrix}M_2'''\\H_3\end{matrix}\right\}O_3$ and $\left.\begin{matrix}M'''\\M'''\end{matrix}\right\}O_3$.

832. *Secondary derivatives.*—The general formula of the anhydrous oxides of the sesqui and tri-atomic metals is $\left.\begin{matrix}M_2'''\\M_2'''\end{matrix}\right\}O_3$ and $\left.\begin{matrix}M'''\\M'''\end{matrix}\right\}O_3$.

833. The sulphides, &c., of these metals are, of course, constructed on the same type, the sulphur, &c., taking the place of the oxygen.

(2.) TRIATOMIC ALCOHOLS.

(*General formula*, $\left.\begin{matrix}C_nH_{2n-1}\\H_3\end{matrix}\right\}O_3$.)

834. Glycerine is the only alcohol belonging to this class which has yet been discovered. As it can be prepared artificially, and the manner in which it is formed is well understood, there can be no doubt that other members of the group will be formed, and it is not unlikely that some may be found to exist either in the vegetable or animal kingdom. The formula of glycerine is $\left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3$.

835. *Properties.*—In its pure state glycerine forms a nearly colourless and very viscid liquid, of specific gravity 1·27, which cannot be made to crystallize; it has an intensely sweet taste, and mixes with water in all proportions; its solution does not undergo the alcoholic fermentation, but when mixed with yeast and kept in a

warm place, it is gradually converted into propionic acid. It has no action upon vegetable colours. Exposed to heat, it volatilizes in part, darkens, and becomes destroyed, acrolein being one of its products of destruction.

836. Glycerine was discovered by Scheele in 1779; he named it "sweet principle of oils," from its sweet taste. The fixed oils and fats are compound ethers; the acids in these ethers belong to the first or second series of the monobasic organic acids; the ether which exists in all oils and fats hitherto examined, with the exception of spermaceti and the different varieties of wax, is the ether of glycerine. Saponification of oils and fats is nothing more than the decomposition, by means of an inorganic base, of these compound ethers; the inorganic base combines with the acids, glycerine being set free. To obtain glycerine by saponification, the inorganic base best adapted for the purpose is oxide of lead, because, by forming with the acids insoluble salts, it separates them completely from the glycerine; and the slight excess of oxide of lead which dissolves in the aqueous solution of the glycerine is easily removed, as sulphide, by adding a little sulphuretted hydrogen. But as glycerine has now become an article of commerce, the scientific chemist has no need to prepare it; it is prepared commercially by separating the acids and the glycerine by superheated steam.

837. Pasteur has shown that glycerine is always formed during the alcoholic fermentation of sugar, to the amount of about 3 per cent. of the sugar decomposed, and that it occurs in all fermented liquors, especially wine.

838. *Preparation.*—Glycerine can be prepared artificially either from terbromide of allyl, or terbromhydrine ($C_3 H_5'' Br_3$), by treating either of these bodies with acetate of silver, bromide of silver and triacetine being formed; glycerine is obtained from triacetine by decomposing this latter substance with baryta water; the liquid is freed from excess of baryta by means of carbonic acid, and evaporated; the residue is treated with anhydrous alcohol, containing a little ether, and the solution thus produced is evaporated. The glycerine then remains in the form of a syrupy liquid, very soluble in alcohol and water, but insoluble in ether.

839. Bromide of bromopropylene, $C_3 H_5 Br' Br_2$, which

is isomeric with terbromide of allyl and terbromhydrine, yields but a very small quantity of triacetine when treated with acetate of silver.

840. *Chemical properties.*—We must keep constantly in mind, in considering the chemical changes which this triatomic alcohol undergoes with many reagents, that it is constructed on the type of three atoms of water, that three out of the six atoms of hydrogen in three atoms of water remain in the alcohol, and that they are capable of being replaced by simple and compound radicals; three series of bodies can, on this account, be obtained from this triatomic alcohol, whilst only two series can be obtained from the biatomic, and one series from the monatomic alcohols.

841. *Substitution of the halogens for the typical hydrogen.*—If glycerine is saturated with hydrochloric acid gas, and the solution is maintained for several hours at 212° F., and if it is neutralized subsequently with carbonate of soda, and agitated with ether, the ether dissolves out an oil-like body, which is left on evaporating the ether; this body has an etherial odour and a sweet taste. It is miscible with water and ether. Its density is 1·31, and it boils at 441° F. It is called monochlorhydrine, and its empirical formula is $C_3H_7ClO_2$; its rational formula is evidently $\left.\begin{matrix}(C_3H_5)''' \\ H_2 \\ Cl\end{matrix}\right\}O_2$. It has already been remarked that three series of bodies could be obtained from glycerine from its containing three replaceable atoms of hydrogen. Monochlorhydrine is a member of the first series of compounds; it is the first stage in the conversion of this alcohol into its normal (ter) chloride,—the first stage in the conversion of a body constructed on the type of three atoms of water into a body constructed on the type of three atoms of hydrochloric acid. In the substitution of the atom of chlorine for the atom of hydrogen, one atom of oxygen is removed along with the hydrogen; so that it is the substitution of one atom of chlorine for an atom of peroxide of hydrogen, or the residue of water. The following equation expresses the reaction:—

$$\left.\begin{matrix}(C_3H_5)''' \\ H \\ H \\ H\end{matrix}\right\}O_3 + HCl = \left.\begin{matrix}(C_3H_5)''' \\ H \\ H \\ Cl\end{matrix}\right\}O_2{}^* + \left.\begin{matrix}H \\ H\end{matrix}\right\}O$$

842. When ten or twelve times its bulk of fuming hydrochloric acid is added to glycerine, and the mixture is exposed for several days to a temperature of 212° F., and then treated as in the preparation of monochlorhydrine, a body is obtained which has a strong etherial odour; it dissolves readily in ether, but with greater difficulty in water than monochlorhydrine; it boils at 352° F. It is called dichlorhydrine; its rational formula is $\left.\begin{matrix}(C_3H_5)''' \\ H \\ Cl \\ Cl\end{matrix}\right\}O$; this is the second series of bodies produced in the process of the transformation of the triatomic alcohol into its terchloride.

843. Pentachloride of phosphorus can be employed in the place of hydrochloric acid, for preparing these bodies.

844. Glycerine is reproduced on treating either monochlorhydrine, or dichlorhydrine, with oxide of lead or the alkalies.

845. When dichlorhydrine is acted upon by pentachloride of phosphorus, trichlorhydrine ($C_3H_5Cl_3$) is obtained.

$$\left.\begin{matrix}(C_3H_5)''' \\ H \\ Cl_2\end{matrix}\right\}O + PCl_5 = C_3H_5Cl_3 + PCl_3O + HCl$$

846. Monobromhydrine and dibromhydrine are obtained by acting upon glycerine with terbromide of phosphorus; and tribromhydrine is obtained by acting upon the dibromhydrine with pentabromide of phosphorus.

847. By acting upon dibromhydrine with pentachloride of phosphorus, we obtain chlordibromhydrine.

848. We will just glance at the two other chlorine compounds obtained from glycerine. The formation of these compounds is very instructive in several points of

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[*] When a halogen takes the place of peroxide of hydrogen (H O), Wurtz and other chemists place the halogen underneath the bracket. They write, for instance, the formula of monochlorhydrine thus, $\begin{matrix}\left.\begin{matrix}(C_3H_5)''' \\ H \\ H\end{matrix}\right\}O_2 \\ Cl\end{matrix}$

view, but especially as showing how triatomic bodies pass into biatomic bodies. If dichlorhydrine is acted upon by hydrochloric acid at 212° F., we obtain a body which has been called epichlorhydrine. The empirical formula of this body is $C_3 H_5 Cl O$. Its rational formula would at first be difficult to determine, were it not for the chlorine compound we are about to notice. It is evident, as the student will see from this body, that epichlorhydrine belongs to the first series of chlorine compounds of a biatomic radical; the one atom of hydrogen which the hydrochloric acid has separated from dichlorhydrine, and thus converted that body into epichlorhydrine, has been at the expense of the radical $C_3 H_5$; and this loss of hydrogen has converted the teratomic radical into a biatomic one. The rational formula, therefore, of epichlorhydrine is

$$\left.\begin{matrix}(C_3 H_4)'\\ H\\ Cl\end{matrix}\right\} O.$$

If we act upon epichlorhydrine with pentachloride of phosphorus, we obtain epidichlorhydrine, which is the bichloride of the diatomic radical, $C_3 H_4$. The formula of epidichlorhydrine is $C_3 H_4 Cl_2$. It must, however, be observed, that if epidichlorhydrine is treated with moist oxide of silver, glycerine is regenerated.

849. *Substitution of the hydrogen by compound monatomic acid radicals.*—It is evident, from what has already been stated, that three series of compound ethers can be formed with glycerine. One series will consist of the replacement of one of the atoms of hydrogen by one atom of a monatomic acid radical; a second series will consist of the replacement of two of the atoms of hydrogen by two atoms of a monatomic acid radical; and a third series will consist of the replacement of the three atoms of hydrogen by three atoms of a monatomic acid radical.

850. The fact has already been stated that oils and fats are compound ethers. Almost all of these glycerides are triacid, that is to say, the three atoms of hydrogen have been replaced by three atoms of a monatomic acid radical, and almost all oils and fats are a mixture of two or more of these glycerides. The natural glycerides have been named by adding to an abbreviation of the name of the acid, the termination *in*. Thus we have *stearin*, *olein*, &c. The artificial combinations of the acid radicals and glycerine (artificial fats) have been named in accordance

with this principle; and the prefixes *mono, di*, and *tri*, express respectively the number of atoms of the acid radical contained in them.

851. Berthelot has prepared artificial fats by keeping a mixture of the hydrated acids and glycerine in close vessels, at a more or less elevated temperature, for some time. Many of them are even formed at the ordinary temperature. The glycerides containing one equivalent of acid are mostly obtained by keeping a mixture of the hydrated acid, with excess of glycerine, at a temperature of 392° F. for some time. The compounds containing two equivalents of acid are obtained by treating glycerine with an excess of acid, and keeping the mixture at a temperature of 392° F. In some cases combination takes place at 212° F.; in other cases the temperature requires to be raised to 527° F.

852. The neutral compounds (those containing three equivalents of acid) are obtained by treating the above compounds with excess of acid, and keeping the mixture at a temperature of from 464° F. to 500° F.

853. In many cases the glycerides may be obtained by saturating a mixture of glycerine and the acid with hydrochloric acid gas, and heating to 212° F.

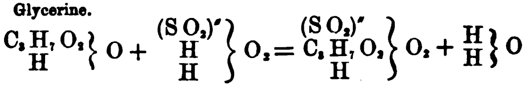
854. We can replace one atom of hydrogen by a compound monatomic acid radical, and one or the two atoms of hydrogen by chlorine or bromine. The first, represented by acetochlorhydrine, $\left.\begin{matrix}(C_3H_5)''' \\ (C_2H_3O) \\ H \\ Cl\end{matrix}\right\} O_2$, is obtained by acting upon glycerine with a chloride of the acid radical. The second, represented by acetodichlorhydrine, $\left.\begin{matrix}(C_3H_5''') \\ (C_2H_3O) \\ Cl_2\end{matrix}\right\} O$, is obtained by acting upon glycerine with the chloride of an acid radical and hydrochloric acid Acetochlorhydrobromhydrine, $\left.\begin{matrix}(C_3H_5)''' \\ (C_2H_3O) \\ Cl \\ Br\end{matrix}\right\} O$, is formed by acting upon every one equivalent of glycerine with an equivalent of the chloride and an equivalent of the bromide

of the acid radical. Diacetochlorhydrine, $\left.\begin{matrix}(C_3H_5)''' \\ (C_2H_3O)_2 \\ Cl\end{matrix}\right\}O_2$, is obtained by acting upon every one equivalent of glycerine with an equivalent of the acid and an equivalent of the chloride of the acid radical.

855. *Formation of acids by the combination of glycerine with polyatomic acid radicals.*—Glycerine, when treated with sulphuric, phosphoric, tartaric acids, &c., combines with them, forming compounds analogous to sulphovinic, phosphovinic, and tartovinic acids.

856. Sulphoglyceric acid is formed by mixing one part of glycerine with two parts of sulphuric acid.

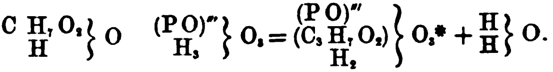
Glycerine.



$$\left.\begin{matrix}C_3H_7O_2 \\ H\end{matrix}\right\}O + \left.\begin{matrix}(SO_2)'' \\ H \\ H\end{matrix}\right\}O_2 = \left.\begin{matrix}(SO_2)'' \\ C_3H_7O_2 \\ H\end{matrix}\right\}O_2 + \left.\begin{matrix}H \\ H\end{matrix}\right\}O$$

Sulphoglyceric acid is monobasic. Example:—Sulphoglycerate of baryta, $\left.\begin{matrix}(SO_2)'' \\ C_3H_7O_2 \\ Ba\end{matrix}\right\}O_2$.

857. Phosphoglyceric acid is formed by mixing glycerine with glacial phosphoric acid.



$$\left.\begin{matrix}C\ H_7O_2 \\ H\end{matrix}\right\}O \quad \left.\begin{matrix}(PO)''' \\ H_3\end{matrix}\right\}O_3 = \left.\begin{matrix}(PO)''' \\ (C_3H_7O_2) \\ H_2\end{matrix}\right\}O_3{*} + \left.\begin{matrix}H \\ H\end{matrix}\right\}O.$$

Phosphoglyceric acid is bibasic. Example:—Phosphoglycerate of baryta, $\left.\begin{matrix}(PO)''' \\ (C_3H_7O_2) \\ Ba_2\end{matrix}\right\}O_3$. A compound of this acid with soda and ammonia is supposed to exist in the yolk of eggs, and in the brain.

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* I do not think that these formulæ are the rational ones for sulpho- and phospho- glyceric acids; I think it is more likely that they are constructed in the following manner, $\left.\begin{matrix}(C_3H_5)''' \\ (SO_2)'' \\ H_3\end{matrix}\right\}O_4$, and $\left.\begin{matrix}(C_3H_5)''' \\ (PO)''' \\ H_4\end{matrix}\right\}O_3$. In like manner the formula of sulpho-glycolic acid will be $\left.\begin{matrix}(C_2H_4)'' \\ (SO_2)'' \\ H_2\end{matrix}\right\}O_3$, instead of $\left.\begin{matrix}(C_2H_3O) \\ (SO_2)'' \\ H\end{matrix}\right\}O_3$. The first two are, I consider, polyglyceric bodies, and the last is a diethylenic body, similar to the succinyl compound.—R. G.

858. Tartroglyceric acid is formed by heating a mixture of equivalent quantities of glycerine and tartaric acid to 150° C.

859. *Substitution of monatomic alcohol radicals for the hydrogen.*—If a mixture of glycerine, caustic potash, and bromide of ethyl is kept at a temperature of 100° for several days, the compound called *diethylene*, $\left(\left.\begin{matrix}(C_3H_5)''\\(C_2H_5)_2\\H\end{matrix}\right\}O_3\right)$ is obtained, in which two equivalents of the hydrogen have been replaced by two equivalents of ethyl. If this body be acted upon by perchloride of phosphorus, chlorhydrodiethylene $\left(\left.\begin{matrix}(C_3H_5)''\\(C_2H_5)_2\\Cl\end{matrix}\right\}O_2\right)$ is obtained; and if this body be kept along with a solution of ethylate of sodium for some hours in a sealed tube, at a temperature of 120° C., we obtain triethylene, $\left.\begin{matrix}(C_3H_5)''\\(C_2H_5)_3\end{matrix}\right\}O_3$.

860. *Substitution of oxygen for some of the hydrogen in the radical.*—"Nitric acid oxidizes glycerine with great ease, the product of the reaction being an acid called glyceric acid.

$$\underset{\text{Glycerine.}}{C_3H_8O_3} + O_2 = \underset{\text{Glyceric acid.}}{C_3H_6O_4} + H_2O$$

Glyceric acid is formed from glycerine in a manner analogous to that of acetic acid from vinic alcohol, or glycolic acid from glycol; two atoms of hydrogen in each of these three alcohols being replaced by one of oxygen. The acid, which stands to glyceric acid in the same relation that oxalic acid does to glycolic acid, or malonic to lactic acid, appears to be the tartronic acid of Dessaignes.

Glycolic acid.	Lactic acid.	Glyceric acid.
$C_2H_4O_3$	$C_3H_6O_3$	$C_3H_6O_4$
Oxalic acid.	Malonic acid.	Tartronic acid.
$C_2H_2O_4$	$C_3H_4O_4$	$C_3H_4O_5$

861. "Although the formation of tartronic acid from glyceric acid has not yet been experimentally established, other properties point out the existence of an intimate connection between these two substances.

862. "The oxidation of propyl-glycol yields, according to the conditions of the experiment, lactic or glycolic acid.

$$\left.\begin{array}{c}(C_3H_6)''\\ H_2\end{array}\right\}O_2 + 2O = C_3H_6O_3 + H_2O$$

$$\left.\begin{array}{c}(C_3H_6)''\\ H_2\end{array}\right\}O_2 + 4O = C_2H_4O_3 + CO_2 + H_2O$$

863. "Glyceric acid may be converted into lactic acid, and tartronic acid into glycolic acid. The transformation of glyceric and tartronic acids, and their composition, support the view, therefore, that they are connected in the same manner as oxalic and glycolic acids.

864. "According to our knowledge of several salts of glyceric acid, this substance appears to be monatomic; but if we consider its derivation from glycerine, the view of M. Wurtz, who considers glyceric acid to be triatomic, is very probably correct.

$$\left.\begin{array}{c}(C_3H_3O)'''\\ H_3\end{array}\right\}O_3\text{, glyceric acid.}$$

This point, however, requires further investigation."—*Debus.*

865. *Formation of glyceramine.*—When monochlorhydrine acts on ammonia, the hydrochlorate of a base called glyceramine is formed, $Cl\left.\begin{array}{c}C_3H_7O_2\\ H_3\end{array}\right\}N$.

866. *Transformation of glycerine into propyl-glycol.*—When an aqueous solution of monochlorhydrine is acted upon at the common temperature with an amalgam of sodium, it is converted into propyl-glycol.

867. *Decomposition of glycerine by potash.*—When glycerine is gently heated with hydrate of potash or soda, it is decomposed, hydrogen is liberated, and acetate and formiate of potash are formed.

868. There can be no doubt that if we were to employ, in place of terbromide of allyl, the iodides, bromides, or chlorides of other triatomic radicals, corresponding triatomic alcohols would be formed.

EXERCISE.

157. Write out the formulæ of the following bodies, and state how you would prepare them:—Monoleine, dibu-

tyrine, monovalerine, tribenzocyine, dipalmytine, tristearine, benzochlorhydrine.

APPENDIX F.

APPENDIX TO GLYCERINE GROUP.

869. Lourenço has quite recently obtained polyglycerines which stand in the same relation to glycerine as the polyethylenic bodies do to glycol. For further information respecting these polyglycerines, the student is referred to the "Répertoire de Chimie Pure," vol. iii., page 147.

NEGATIVE GROUP.

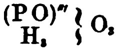
870. This group embraces—(1) The mineral triatomic acids. (2) The organic triatomic acids, and the salts of these acids.

TRIATOMIC ACIDS.

871. The substitution of a triatomic acid radical for three atoms of hydrogen in three molecules of water, produces a triatomic acid.

872. Tribasic acids are not volatile without decomposition. They can form three classes of salts, according as they exchange one, two, or three atoms of hydrogen for a metal. Examples:—

Phosphoric acid.

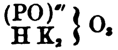


$$\left.\begin{matrix}(PO)'''\\ H_3\end{matrix}\right\} O_3$$

Primary phosphate of potash.

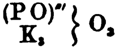
$$\left.\begin{matrix}(PO)'''\\ H_2\,K\end{matrix}\right\} O_3$$

Secondary phosphate of potash.



$$\left.\begin{matrix}(PO)'''\\ H\,K_2\end{matrix}\right\} O_3$$

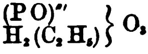
Tertiary phosphate of potash.



$$\left.\begin{matrix}(PO)'''\\ K_3\end{matrix}\right\} O_3$$

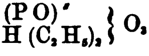
873. These acids can give with each alcohol three ether salts, one of which is neutral, and the other two are acid. Examples:—

Primary phosphoric ethyl-ether.



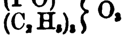
$$\left.\begin{matrix}(PO)'''\\ H_2\,(C_2H_5)\end{matrix}\right\} O_3$$

Secondary phosphoric ethyl-ether.



$$\left.\begin{matrix}(PO)'\\ H\,(C_2H_5)_2\end{matrix}\right\} O_3$$

Tertiary phosphoric ethyl-ether.



$$\left.\begin{matrix}(PO)'''\\ (C_2H_5)_3\end{matrix}\right\} O_3$$

874. *Considered in the state of vapour, under the same volume, the neutral ethers (tertiary ethers) of the tribasic acids contain three times the amount of the alcohol radical which the neutral ethers of the monobasic acids contain.*

875. The ammoniacal salts of the tribasic acids are not volatile without decomposition. Their amides are still little known; however, we have already obtained some acid amides and diamides which correspond to the tribasic acids.

876. *Considered in the state of vapour, under the same volume, the chlorides of the tribasic acids contain three times the amount of chloride which the chlorides of monobasic acids contain.*

(1.) MINERAL ACIDS.

877. The following are the principal tribasic inorganic acids:—

	Primary derivatives.	Secondary derivatives.	
Phosphorous acid -	$\left.\begin{matrix}P''' \\ H_3\end{matrix}\right\} O_3$	Phosphorous anhydride - -	P_2O_3
Phosphoric acid* -	$\left.\begin{matrix}(PO)''' \\ H_3\end{matrix}\right\} O_3$	Phosphoric anhydride - -	P_2O_5
Arsenious acid -	$\left.\begin{matrix}As''' \\ H_3\end{matrix}\right\} O_3$	Arsenious anhydride - -	As_2O_3
Arsenic acid -	$\left.\begin{matrix}(AsO)''' \\ H_3\end{matrix}\right\} O_3$	Arsenic anhydride - -	As_2O_5
Boracic acid -	$\left.\begin{matrix}B''' \\ H_3\end{matrix}\right\} O_3$	Boracic anhydride - -	B_2O_3

(2.) ORGANIC ACIDS.

878. Only a small number of triatomic organic acids is known.†

FIRST CLASS.

879. Glyceric acid appears to be monobasic, but its salts have as yet been but little investigated. From its derivation from the triatomic body, glycerine, it must be triatomic, and it will bear the same relation to one or perhaps two series of acids which lactic acid bears to the oxalic. Its formula, represented as a triatomic acid, is $\left.\begin{matrix}(C_3H_3O)''' \\ H_3\end{matrix}\right\} O_3$.

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* The composition of the pyrophosphates is $M_4P_2O_7$; they may be viewed as formed by the union of an atom of orthophosphate with an atom of metaphosphate.

† Dr. Maxwell Simpson has quite recently obtained a tribasic acid by acting upon tercyanide of allyl with potash.

SECOND CLASS.

880. There must be an acid standing to glyceric acid in the same relation as oxalic acid stands to glycolic acid, and the acid must be triatomic, and probably will be tribasic. Debus thinks that tartronic acid occupies this relation. This acid as yet has only been prepared from the spontaneous decomposition of nitro-tartaric acid. It forms a neutral and acid salt with ammonia; it has therefore been considered to be bibasic, and homologous with malic acid; but if the view of Debus be correct, it must be a triatomic acid. Its formula would, in accordance with this view, be $\left.\begin{matrix}(C_3HO_2)'''\\ H_3\end{matrix}\right\}O_3$.

FOURTH CLASS.

881. We shall merely give the names and formulæ of the following acids:—

Citric acid	$\left.\begin{matrix}(C_6H_5O_4)'''\\ H_3\end{matrix}\right\}O_3$
Aconitic acid	$\left.\begin{matrix}(C_6H_3O_3)'''\\ H_3\end{matrix}\right\}O_3$
Meconic acid	$\left.\begin{matrix}(C_7HO_4)'''\\ H_3\end{matrix}\right\}O_3$
Chelidonic acid . . .	$\left.\begin{matrix}(C_7HO_3)'''\\ H_3\end{matrix}\right\}O_3$

882. The anhydrides of these acids have not been obtained.

EXERCISE.

158. Write out the formulæ of the following salts and ethers:—Primary phosphate of potassium, secondary citrate of sodium, tertiary phosphate of calcium, primary phosphoric ethyl-ether (monethyl phosphoric acid), tertiary phosphoric ethyl-ether (neutral phosphate of ethyl), secondary phosphoric ethyl-ether (biethyl phosphoric acid), biethyl citric acid.

QUADRUPLE MOLECULE.

$$\left.\begin{matrix}H_4\\ H_4\end{matrix}\right\}O_4.$$

883. The only body we shall notice under this type is silicic acid.

884. Dr. Odling has recently directed attention to the basicity of silicic acid. He regards this acid as a tetrabasic acid, and he bases this opinion upon the following facts:—"We are acquainted with various binary compounds of hydrogen, and with certain quadroxy acids and salts indirectly procurable from them, thus:—

Chlorhydric acid	- HCl	$HClO_4$	- Perchloric acid
Sulphydric acid	- H_2S	H_2SO_4	- Sulphuric acid
Phosphamine	- H_3P	H_3PO_4	- Phosphoric acid

And it seems to be a general rule, that binary hydrides, with one, two, three, or more atoms of hydrogen, yield quadroxy acids and salts, with an equal number of atoms of hydrogen, or equivalents of basic metals, respectively."

885. If one equivalent of water (H_2O) is removed from the phosphoric acid, we obtain what is termed metaphosphoric acid, and as this acid has, like perchloric acid, only one atom of basic hydrogen, it is, like that acid, monobasic, it unites only with one atom of base. Now the tribasic salts we shall term orthophosphates,* and the monobasic ones metaphosphates.

886. Between the meta and ortho-phosphates there is an intermediate class, which may be viewed as composed of an atom of each of the two salts named, viz., meta and ortho-salts.

$$M_3PO_4 + MPO_3 = M_4P_2O_7$$

887. When phosphoric anhydride (P_2O_5) is fused with a salt, it depends upon the facility with which the anhydride of that salt can be driven off, whether we obtain an ortho, meta, or intermediate phosphate. Thus, Dr. Odling finds that when sulphate of magnesium is heated with phosphoric anhydride, orthophosphate of magnesium (Mg_3PO_4) is produced, because sulphuric anhydride is somewhat readily expelled from magnesia; but when phosphoric anhydride is fused with sulphate of potassium, only metaphosphate of potassium (KPO_3) is produced, because sulphuric anhydride is powerfully retained by potassa. The phosphoric acid obtained from the magnesium salt gave a yellow precipitate with ammonio-nitrate of silver, and did not coagulate albumen. The phosphoric

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* For an explanation of this term, see par. 707.

acid obtained from the potash salt gave a white precipitate of nitrate of silver, and did coagulate albumen.

888. "The case of silicic acid appears to be precisely similar to that of phosphoric acid. In default of a correct knowledge of the composition of siliciuretted hydrogen, we rely upon our acquaintance with chloride of silicon. The vapour-density of this compound requires the existence of four atoms of chlorine within its two-volume molecule, and its formula is, consequently, $Si\,Cl_4$, with which expression, moreover, its reactions best accord. Corresponding to this chloro-derivative of a tetrahydride of silicon, we ought to have a class of tetrabasic, quadroxy orthosilicates, having the general formula $M_4\,Si\,O_4$, and constituting the fourth term of the following series:—

Perchlorates - -	$M\,Cl\,O_4$
Sulphates - -	$M_2\,S\,O_4$
Phosphates - -	$M_3\,PO_4 - M_2O = M\,PO_3$
Silicates - -	$M_4\,SiO_4 - M_2O = M_2\,SiO_3$

889. Precisely as the tribasic are the most highly basic of the phosphates, so are the tetrabasic the most highly basic of the silicates; and as the tribasic orthophosphates, by the loss of an atom of base, M_2O, become monobasic metaphosphates, so do the tetrabasic orthosilicates, by the loss of an atom of base, $M_2\,O$, become bibasic metasilicates; and as there are intermediate or pyrophosphates, with seven atoms of oxygen, so are there intermediate [illegible] silicates with seven atoms of oxygen; and as phosphoric anhydride, when fused with a salt of a volatile anhydride, may form an ortho, meta, or intermediate phosphate, according to the facility with which the volatile anhydride is liberated, so does silicic anhydride, when fused with the salt of a volatile anhydride, yield an ortho, meta, or intermediate silicate, according to the facility with which the volatile anhydride is liberated. Carbonate of lithium evolves carbonic anhydride more readily than does carbonate of potassium, while carbonate of sodium is, in this respect, intermediate between the two. Hence, when Colonel York fused silica with each of these alkaline carbonates, he obtained with carbonate of lithium an orthosilicate ($Li_4\,SiO_4$); with carbonate of potassium he obtained a metasilicate ($K_2\,Si\,O_3$); whilst with carbonate of sodium he obtained an intermediate silicate ($Na_6\,Si_2\,O_7$

$= Na_4SiO_4 + Na_2SiO_3$);[*] and it will be found that all non-aluminous silicates, which do not contain an excess of *silicic anhydride*, may be referred to one or other of the three types,—

$$M_4SiO_4\text{, orthosilicate} = 2\,M_2O, SiO_3$$
$$M_2SiO_3\text{, metasilicate} = M_2O, SiO_2$$
$$M_6Si_2O_7\text{, } \tfrac{3}{2}\text{ silicate} = 3\,M_2O, 2\,SiO_2$$

890. "If we consider alumina as always basic, then there are silicates in which the basicity exceeds that of the tetrabasic group; but the basic, or acidulous function of alumina in many minerals is yet *sub judice;* and if we exclude aluminous minerals, we shall find that the tetrabasic are the most highly basic of all known silicates, natural or artificial. As illustrating the existence of the above three classes of silicates, I append the following lists, which are capable of considerable extension. It is observable, however, that the ortho-silicates are far more numerous than either the meta or $\frac{3}{2}$ silicates; that they are, in fact, the normal salts, both as regards constitution and distribution.

CLASS I.—*Orthosilicates.*

Type, M_4SiO_4, corresponding to M_3PO_4, orthophosphate.

Et_4SiO_4	Silicic ether (2 vols.)
Li_4SiO_4	Orthosilicate of lithium
Na_4SiO_4	Orthosilicate of sodium
Ca_4SiO_4	Orthosilicate of calcium
Mg_4SiO_4	Olivine, chrysolite
$Ca_2Mg_2SiO_4$	Batrachite
Zn_4SiO_4, H_2O	Zinc glance
Gl_4SiO_4	Phenakite
Y_4SiO_4	Gadolinite
Ce_4SiO_4	Cerite
Z_4SiO_4	Zircon
Mn_4SiO_4	Orthosilicate of manganese
$Mn_2Gl_2SiO_4$	Helvine
Fe_4SiO_4	Fayelite, forge-cinder
$(MgFe)_4SiO_4$	Hyalosiderite

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[*] "Philosophical Transactions," 1857.

$Fe_2 Mn_2 Si O_4$ - -	Knebelite
$\mathit{fe}_4 Si O_4$ - - -	Yellow earth
$(\mathit{fe}\ Fe\ Ca)_4 Si O_4$ - -	Ilvaite
$Cu_2 H_2 Si O_4$ - - -	Dioptase
$\mathit{al}_4 Si O_4$ - - -	Bucholzite
$\mathit{Al}_2 Ca_2 Si O_4$ - -	Garnet, idocrase, vesuvian
$\mathit{al}_3 Ca Si O_4$ - - -	Wernerite, anorthite
$\mathit{al}_3 (Ca Na)' Si O_4$ - -	Thomsonite
$\mathit{Al}_3 Mn Si O_4$ - -	Karpholite

891. "In addition to these comparatively simple orthosilicates, which can readily be formulated, there are a great number of complex silicates, containing mixtures of several bases, proto-equivalent and sesqui-equivalent, which evidently pertain to the formula, $M_4 Si O_4$, or $M_2 O, Si O_2$, because, despite great variations in composition, the ratio of the oxygen in the base to the oxygen in the anhydride invariably equals $\frac{1}{2}$. Such, for instance, are harmatome, prehnite, chabasite, mesotype, &c.

CLASS II.—*Metasilicates.*

Type, $M_2 Si O_3$, corresponding to $M P O_3$, metaphosphate.

$K_2 Si O_3$ - -	Metasilicate of potassium
$Na_2 Si O_3, H_2 O$ - -	Metasilicate of sodium
$Ca_2 Si O_3$ - - -	Wollastonite
$Mg_2 Si O_3$ - - -	Picrosmine, aphrodite
$Ca Mg Si O_3$ - - -	Augite
$(Ca Mg Fe)_2 Si O_3$ - -	Diallage
$Fe_2 Si O_3$ - - -	Iron slag
$Mn Fe Si O_3$ - - -	Pyrosmalite
$\mathit{Al}_2 Si O_3, H_2 O$ - -	Clay
$\mathit{fe}_2 Si O_3$ - - -	Nontronite
$Cu_2 Si O_3, H_2 O$ - -	Chrysocolla

CLASS III.—$\frac{3}{2}$ *Silicates.*

Type, $M_6 Si_2 O_7$, corresponding to $M_4 P_2 O_7$, pyrophosphates.

$Na_6 Si_2 O_7$ - - -	Silicate of sodium
$Mg_6 Si_2 O_7$ - - -	Ophite, noble serpentine
$\mathit{al}_6 Si_2 O_7$ - - -	Clay
$(\mathit{al}\ Mg\ Fe)_6 Si_2 O_7$ - -	Cordierite

$Ca_4\,al_2\,Si_2\,O_7$	Sarcolite
$Fe_6\,Si_2\,O_7$	Iron slag
$fe_6\,Si_2\,O_7,\,H_2\,O$	Hisingerite
$Fe_2\,al_4\,Si_2\,O_7,\,H_2\,O$	Ottrelite

892. "From the foregoing lists, we perceive that phosphates and silicates are strictly comparable with one another; but a comparison of the phosphoric acids with their corresponding silicic acids is impossible, from our ignorance of the constitution and properties of the latter acids, if indeed they have any existence; but we should not, I think, expect to observe any decided differences in the three modifications, seeing that even in the phosphoric acids, despite the facilities afforded by their soluble condition, the distinctions are not of a highly characteristic kind. We might even speculate upon what our knowledge of the varieties of phosphoric acid would now have been, if orthophosphate of silver had chanced to be of a white instead of a yellow colour."

893. Dr. Odling then enters upon the relations of nitrates and phosphates to carbonates and silicates respectively, but we must refer the student to the original paper.*

CHAPTER IX.

HYDROCHLORIC ACID TYPE.

894. The substances grouped under each molecule are subdivided into positive chlorides and negative chlorides.

SIMPLE MOLECULE.

$H\,Cl$.

POSITIVE CHLORIDES.

895. This group embraces—(1) The chlorides, &c., of the monatomic metals. (2) The chlorides, &c., of the mononium bodies. (3) The chlorides, &c., of the monatomic alcohol radicals. (4) The chlorides, &c., of the vinyl series.

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* "Dr. Odling on Ortho and Meta-Silicates."—*Philosophical Magazine* 1857. The student might also consult with advantage a paper by Dr. Odling on Acids and Salts, in vol. i. of the *Chemical News*.

(1.) Chlorides of the Positive Metals.

896. All those metals which we have given under the simple molecule of hydrogen (H, H) as monatomic, are capable, of course, of forming chlorides on the type of a single molecule of chlorhydric acid (H Cl); and as bromhydric, iodhydric, fluorhydric, and cyanhydric acids are formed on the type of chlorhydric acid, these monatomic metals form also bromides, iodides, fluorides, and cyanides, on the type of a simple molecule of chlorhydric acid, thus:—

$$KBr;\ FeCy;\ PtCl;\ AuCl.$$

897. The diatomic metals, $\underset{\prime}{\mathrm{Cu}}$ and $\underset{\prime}{\mathrm{Hg}}$, form, of course, chlorides, bromides, &c., on the type of a single molecule of H Cl, two atoms of the metal replacing one atom of hydrogen, thus:—

$$Cu_2Cl;\ Hg_2Cy.$$

(2.) Chlorides, etc., of the Mon-onium Bodies.*

898. We shall hereafter see how the iodides, bromides, &c., of the primary, secondary, and tertiary ammonium derivatives are prepared, and also how the iodides of the tetra-compounds are formed.

EXERCISE.

159. Write out the formula of chloride of amyl-ammonium,† bromide of biethyl-ammonium, iodide of triethyl-ammonium, and chloride of methy-ethyl-amyl-tolyl-ammonium.

899. The iodides, bromides, and chlorides of the tetra compounds are decomposed by heat into the iodides, bromides, or chlorides of an alcohol radical and a tertiary monamine. When these iodides are thus decomposed, the two substances into which they are decomposed, the iodide of the alcohol radical and the amine, rapidly unite

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[*] This group, mon-onium bodies, must not be commenced until the student has studied the monamines and monamides.

[†] The combinations of the halogens with the primary, secondary, and tertiary ammonium derivatives are frequently designated as if they were combinations of these with the hydrogen acids; thus, instead of chloride of amyl-ammonium, this body would be named hydrochlorate of amylamine.

again; they combine even in the neck of the retort. The chlorides, bromides, and iodides of the tertiary, secondary, and primary monammoniums, undergo by heat analogous decompositions; a chloride, bromide, or iodide of an alcohol radical being formed in the decomposition of each class of salts, and a secondary monamine being formed in the decomposition of the tertiary monammoniums, a primary monamine in the case of the secondary ammoniums, and ammonia in the case of the primary monammoniums.

EXERCISE.

160. Into what substances is chloride of tetrethyl-ammonium, and into what substances is iodide of triamyl-ammonium, and into what substances is bromide of diethyl-ammonium, and into what substances is chloride of methyl-ammonium, decomposed by heat?

900. We have already noticed how the iodides, &c., of phosphoniums, of the arsoniums, and of the stiboniums are formed. The formation of some metal-organo bodies here claims our attention. If to an alcoholic solution of the triethyl compound of phosphorus, arsenic, or of antimony, bichloride of platinum be added, the colour of the platinum solution disappears; if the platinum compound be added as long as this takes place, the liquid, after the reaction is complete, will deposit in a few moments magnificent slightly yellow or colourless crystals. This body is a compound ammonium salt, having P, As, or Sb, in the place of N, and three equivalents of C_2H_5 in place of three equivalents of H, the fourth equivalent of H being replaced by platinum. Terchloride of gold produces a series of similar gold compounds, which are easily obtained in beautiful colourless crystals. Both the platinum and gold compounds are generated with simultaneous formation of the dichlorides of the bases, thus:—

$$3\Big((C_2H_5)_3P\Big)+2PtCl_2=2\Big(\overset{\text{Chloride of platotriethyl-phosphonium.}}{\Big[Pt(C_2H_5)_3P\Big]Cl}\Big)+(C_2H_5)_3PCl_2$$

EXERCISES.

161. Write out the formulæ for iodide of tetramethyl-phosphonium, for chloride of platotriethyl-arsonium, for bromide of tetrethyl-stibonium.

162. State how you would prepare the chloride of aurotriethyl-stibonium, and explain the formation by an equation.

901. The metal ammoniums we shall pass over. We refer the student who wishes to become acquainted with these bodies to Dr. Hoffmann's paper on ammonia and its derivatives, in vols. xi. and xii. of the Chemical Society's Journal.*

(3.) CHLORIDES, ETC., OF THE MONATOMIC ALCOHOL RADICALS.

FIRST CLASS.

(*General formula*, $C_n H_{2n+1} Cl$.)

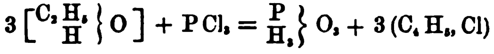
EXERCISE.

902. Write out the formulæ of the following compounds:—Chloride of methyl, iodide of amyl, cyanide of ethyl, bromide of hexyl, cyanide of tetryl.

903. *Preparation of the chlorides of this class of alcohol radicals.*—These chlorides are obtained by saturating the alcohols with dry hydrochloric acid gas, and distilling off the chloride which is formed at a very gentle heat; or they may be obtained by pouring a mixture of three parts of oil of vitriol and two of the alcohol upon four parts of dry chloride of sodium in a retort, and then applying heat. In either case the vapour of the ether chloride should be conducted through a little tepid water in a wash bottle, and then conveyed into a small receiver surrounded by ice and salt. It is purified from adhering water by contact with a few fragments of fused chloride of calcium.

904. They may also be obtained by the action of one of the chlorides of phosphorus upon the alcohols, thus:—

Vinic alcohol. Phosphorous acid. Chloride of ethyl.



$$3\left[\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O\right] + PCl_3 = \left.\begin{matrix}P\\H_3\end{matrix}\right\}O_3 + 3(C_4H_5, Cl)$$

905. *Properties of these chlorides.*—These ethers are gaseous (chloride of methyl), liquid, or solid bodies (chloride of cetyl). They are more volatile than the corresponding

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* When the student has gone through this group, he commences the group of the hydrated oxides of the mon-oniums (par. 547.)

alcohols. They are generally more stable than the corresponding bromides, and especially than the corresponding iodides. The chlorine in these chlorides is not precipitated by nitrate of silver; possibly it might be by freshly precipitated oxide of silver. When any one of these chlorides is treated with sodium in the cold, chloride of sodium and the alcohol metal corresponding to the ether employed are produced; but when the reaction is assisted by heat, hydrogen is disengaged, chloride of sodium produced, and a hydrocarbon of the general formula $C_n H_{2n}$. An alcoholic solution of potash decomposes these chlorides into chloride of potassium and the corresponding alcohol, thus:—

$$C_2H_5Cl + \left.\begin{matrix}K\\H\end{matrix}\right\}O = KCl + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$$

906. By the prolonged action of chlorine, the hydrogen in the alcohol radical can be successively replaced by equal equivalents of chlorine. Example:—

Chloride ethyl (hydrochloric ether) -	$C_2H_5\}Cl$
Monochlorinated chloride of ethyl -	$C_2H_4Cl\}Cl$
Bichlorinated chloride of ethyl - -	$C_2H_3Cl_2\}Cl$
Trichlorinated chloride of ethyl - -	$C_2H_2Cl_3\}Cl$
Tetrachlorinated chloride of ethyl -	$C_2HCl_4\}Cl$
	$C_2Cl_5\}Cl$

907. The bichlorinated chloride of methyl, $CHCl_2Cl$, is chloroform.

908. *Preparation of the bromides of these radicals.*—They are usually prepared by adding, by degrees, seven or eight parts of bromine to forty parts of alcohol and one part of phosphorus, contained in a retort; a very moderate heat is applied, and the product which distils over is collected in a cooled receiver. It is purified by agitation with a weak solution of potash, which removes the alcohol and the traces of hydrobromic acid with which it is contaminated. The purified ether is then digested upon chloride of calcium, and subsequently distilled. The changes which take place are these:—The bromine and phosphorus unite and produce bromide of phosphorus, which compound is decomposed by the water in the alco-

hol into phosphorous acid and hydrobromic acid; the nascent hydrobromic acid forms, with the alcohol, water and the bromide of the alcohol radical.

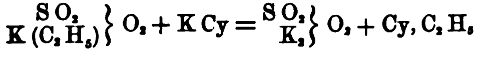
909. *Properties of these bromides.*—They are less volatile than the corresponding chlorides, which they resemble in their other physical characters, and in their chemical reactions. With ammonia and the amines they unite, forming the bromide of the corresponding ammonium.

910. *Preparation of the iodides of these radicals.*—The iodides are prepared in the same way as the bromides.

911. *Properties of the iodides.*—They are less volatile than the corresponding chlorides; they are also less stable. We have already seen that they are decomposed by tin and other metals, iodides of the metals being formed, and the organic radicals set free. We shall hereafter see that Hofmann has employed them extensively in forming the compound ammonias, and also in determining the constitution of compound ammonias. Unlike the corresponding chlorides, these iodides are decomposed by nitrate of silver, iodide of silver being formed, whilst the alcohol radical combines with the nitric acid.

912. *Preparation of the cyanides of these radicals.*—These cyanides can be obtained in two essentially different ways,—(1) By distilling a sulphovinate or homologous salt with cyanide of potassium, thus:—

Sulphovinate of potassium. Sulphate of potassium. Cyanide of ethyl.

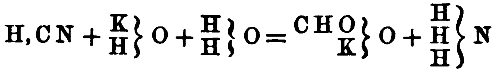


$$\left.\begin{matrix}\mathrm{S\,O_2}\\\mathrm{K\,(C_2H_5)}\end{matrix}\right\}\mathrm{O_2} + \mathrm{K\,Cy} = \left.\begin{matrix}\mathrm{S\,O_2}\\\mathrm{K_2}\end{matrix}\right\}\mathrm{O_2} + \mathrm{Cy, C_2H_5}$$

2nd Method.—By heating with the dehydrating agent phosphoric anhydride, the ammonia salts of the acids formed out of these alcohol radicals, or the amides of the acid radicals: this method we shall hereafter consider, in viewing these cyanides as tertiary monamides.

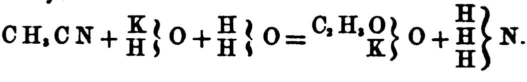
913. *Properties of these cyanides.*—Submitted to the action of acids and alkalies they fix two atoms of water, and there is reproduced ammonia and the acid from the ammonium salt, of which they can be formed when it is made to lose two equivalents of water. Examples:—

Hydrocyanic acid. Formiate of potash.

(1)


$$H,CN + \left.\begin{matrix}K\\H\end{matrix}\right\} O + \left.\begin{matrix}H\\H\end{matrix}\right\} O = \left.\begin{matrix}CHO\\K\end{matrix}\right\} O + \left.\begin{matrix}H\\H\\H\end{matrix}\right\} N$$

Cyanide of methyl.

(2)


$$CH_3CN + \left.\begin{matrix}K\\H\end{matrix}\right\} O + \left.\begin{matrix}H\\H\end{matrix}\right\} O = \left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\} O + \left.\begin{matrix}H\\H\\H\end{matrix}\right\} N.$$

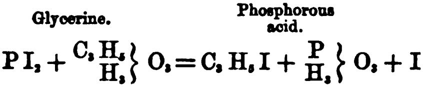
914. The action of potassium upon cyanide of ethyl is remarkable. If the ether be allowed to fall drop by drop upon potassium contained in a flask fitted to a vertical condenser, by means of which any part of the ether which escapes decomposition is allowed to fall back upon the potassium, hydride of ethyl is formed, whilst cyanide of potassium is produced, and an alkaline base, termed cyanethine ($C_{18} H_{15} N_3$), remains in the flask. This base is polymeric with cyanide of ethyl. It crystallizes from boiling water in pearly scales, and forms salts with the acids. The other hydrocyanic ethers, when treated with potassium, appear to furnish compounds analogous to cyanethine.

CHLORIDES, ETC., OF THE MONATOMIC ALCOHOL RADICALS FORMING THE SECOND CLASS.

(*General formula*, $C_n H_{2n-1} Cl$.)

915. *Preparation.*—The chloride, bromide, and iodide of allyl are readily obtained by distilling allyl-alcohol with the chloride, bromide, and iodide of phosphorus. The chloride and bromide of allyl have also been prepared from one of the hydro-carbons, which is formed in the destructive distillation of amylic alcohol. The vapour of vinic alcohol is entirely decomposed into olefiant gas ($C_2 H_4$), and marsh gas ($C H_4$), on passing it through a red-hot tube. Capt. Reynolds subjected the vapour of amylic alcohol to a similar treatment, expecting, of course, to get the corresponding hydro-carbons, $C_5 H_{10}$, and $C_4 H_{10}$, but he obtained a gas having the formula $C_3 H_6$, which combined with bromine and chlorine, forming in each case an oily liquid, having the formula $C_3 H_6 Br_2$, and $C_3 H_6 Cl_2$: these bodies, when treated with an alcoholic solution of potash, behaved like the members of the

olefiant gas series, the elements of hydrobromic acid and hydrochloric acid separated, and C_3H_5Br, and C_3H_5Cl, bromide and chloride of allyl, remained. Iodide of allyl is formed when equal parts of crystallized biniodide of phosphorus, PI_2, and the teratomic alcohol glycerine, are distilled; the C_3H_5I distils over, thus:—



$$PI_2 + \overset{\text{Glycerine.}}{\left.\begin{matrix} C_3H_5 \\ H_3 \end{matrix}\right\} O_3} = C_3H_5I + \overset{\text{Phosphorous acid.}}{\left.\begin{matrix} P \\ H_3 \end{matrix}\right\} O_3} + I$$

A considerable volume of pure gaseous tritylene is also formed in the reaction, but its formation appears to be due to a secondary action. Iodide of allyl, when distilled with mercury and concentrated hydrochloric acid, furnishes a ready means to obtain pure tritylene:—

$$C_3H_5I + HCl + 4Hg = C_3H_6 + Hg_2I + Hg_2Cl$$

916. Cyanide of allyl has lately been prepared.

CHLORIDES, ETC., OF THE MONATOMIC ALCOHOL RADICALS FORMING THE THIRD CLASS.

(*General formula*, $C_nH_{2n-7}Cl$.)

917. *Preparation.*—The chlorides, bromides, and iodides of these radicals are obtained by distilling their alcohols with the chloride, bromide, and iodide of phosphorus.

918. The cyanides may be prepared by the distillation of the ammonium salts of their corresponding acids.

APPENDIX G.

(4). CHLORIDES, ETC., OF THE MONATOMIC RADICALS OBTAINED FROM THE OLEFIANT GAS SERIES.

(*General formula*, $C_nH_{2n-1}Cl$.)

919. When the chlorides, iodides, or bromides of the biatomic radicals of the olefiant gas series are treated with an alcoholic solution of potash, hydrochloric, hydrobromic, or hydriodic acid separates, and there remains a mon-

atomic radical, having the general formula $C_n H_{2n-1}$, in combination with chlorine, bromine, or iodine.

920. The one having the formula C_2H_3Cl is named chloride of acetyl, or chloride of vinyl.

NEGATIVE CHLORIDES.

921. This group embraces—(1) The hydrogen compounds of monatomic elements, or radicals, analogous to chlorine. (2) The chlorides of the radicals of the oxygen acids.

(1.) CHLORIDES, ETC., OF THE HALOGEN GROUP OF ELEMENTS AND OF CYANOGEN.

922. The halogen group of elements unite with hydrogen, and form bodies constructed on the type of a single molecule of hydrogen. The hydrogen compound of cyanogen is also constructed on the type of hydrochloric acid; but cyanogen is not only monatomic but also biatomic and triatomic, and therefore we have hydrogen compounds of cyanogen constructed on one, two, and three molecules of hydrochloric acid.

(2.) CHLORIDES, ETC., OF THE RADICALS OF THE OXYGEN ACIDS.

923. If chlorine be substituted for the typical hydrogen in aldehydes, the chlor-aldehyds, or the chlorides of the acid-radicals, are obtained. "The chlor-aldehyds react with water to exchange Cl for peroxide of hydrogen, HO, so as to form chlorhydric acid, and the normal oxacids to which they correspond.

$$
\begin{array}{llcll}
 & \text{Chlor-aldehyds.} & & & \text{Acids.} \\
\text{Nitric - -} & \overbrace{Cl\,NO_2} + H_2O & = & HCl + & \overbrace{H\,NO_3 \text{ or } (HO)\,NO_2} \\
\text{Sulphuric -} & Cl_2SO_2 + 2H_2O & = & 2HCl + & H_2SO_4 \text{ or } (HO)_2SO_2 \\
\text{Phosphoric -} & Cl_3PO + 3H_2O & = & 3HCl + & H_3PO_4 \text{ or } (HO)_3PO
\end{array}
$$

924. "It is observable that the conversion of normal aldehyds into acids by oxidation, may be represented as an exchange of hydrogen, H, for peroxide of hydrogen. Thus, the reactions of chloro and normal acetic aldehyds, upon water and peroxide of hydrogen respectively, may be written in the following corresponding manner:—

$$\left.\begin{array}{l} Cl,C_2H_3O + \left\{\begin{array}{l} H \\ HO \end{array}\right. = \left.\begin{array}{l} H \\ Cl \end{array}\right\} + HO,C_2H_3O \\ H,C_2H_3O + \left\{\begin{array}{l} HO \\ HO \end{array}\right. = \left.\begin{array}{l} HO \\ H \end{array}\right\} + HO,C_2H_3O \end{array}\right\} \text{or, } C_2H_4O_2$$

925. "The chlor-aldehyds bear to their corresponding acids the same relations that metallic chlorides bear to metallic hydrates, and may be represented accordingly, thus :—

$$\begin{array}{lll} \textbf{Chlorides.} & \multicolumn{2}{c}{\overbrace{\textbf{Chlor-aldehyds.}}} \\ Zn'Cl & \left\{\begin{array}{l} (C_2H_3O)'Cl \\ (NO_2)'Cl \end{array}\right. & \begin{array}{l} \text{Acetic} \\ \text{Nitric} \end{array} \\ Pt''Cl_2 \;\; - & (SO_2)''Cl_2 & \text{Sulphuric} \\ Bi'''Cl_3 \;\; - & (PO)'''Cl_3 & \text{Phosphoric} \end{array}$$

$$\begin{array}{lll} \textbf{Hydrates.} & \multicolumn{2}{c}{\overbrace{\textbf{Acids.}}} \\ \left.\begin{array}{l} Zn' \\ H \end{array}\right\} O & \left\{\begin{array}{l} \left.\begin{array}{l} (C_2H_3O)' \\ H \end{array}\right\} O \\ \left.\begin{array}{l} (NO_2)' \\ H \end{array}\right\} O \end{array}\right. & \begin{array}{l} \text{Acetic} \\ \text{Nitric} \end{array} \\ \left.\begin{array}{l} Pt'' \\ H_2 \end{array}\right\} O_2 \;\; - & \left.\begin{array}{l} (SO_2)'' \\ H_2 \end{array}\right\} O_2 & \text{Sulphuric} \\ \left.\begin{array}{l} Bi''' \\ H_3 \end{array}\right\} O_3 \;\; - & \left.\begin{array}{l} (PO)''' \\ H_3 \end{array}\right\} O_3 & \text{Phosphoric} \end{array}$$

As if the molecular groupings, C_2H_3O, NO_2, SO_2, PO, &c., were, like zinc, platinum, bismuth, &c., proto, bi, and ter, equivalents respectively."

926. The acid or negative chlorides are monatomic, biatomic, or triatomic, according to the acids from which they are derived.

MONATOMIC ACID CHLORIDES.

927. In place of giving a list of these acid chlorides, we shall require the student to give the formulæ of these bodies.

928. *Preparation.*—We have already, in par. 393, described the methods by which these bodies are obtained; we may here add, that they may sometimes be obtained direct from aldehydes by substituting chlorine for the typical hydrogen.

929. *Properties.*—These bodies are generally volatile

fuming liquids. They are remarkable for the facility with which they are transformed in contact with water or its derivatives (alcohol, alkalies, alkaline salts), or in contact with ammonia and its derivatives.

1st. In contact with water they are transformed into monobasic acids:—

Chloride of othyl.

$$C_2H_3O,Cl + \left.\begin{matrix}H\\H\end{matrix}\right\}O = \left.\begin{matrix}(C_2H_3O)\\H\end{matrix}\right\}O + HCl$$

2nd. With the alkalies they behave in a corresponding manner:—

$$C_2H_3O,Cl + \left.\begin{matrix}K\\K\end{matrix}\right\}O = \left.\begin{matrix}(C_2H_3O)\\K\end{matrix}\right\}O + KCl$$

3rd. With the alcohols they give compound ethers:—

$$C_2H_3O,Cl + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O = \left.\begin{matrix}(C_2H_3O)\\(C_2H_5)\end{matrix}\right\}O + HCl$$

4th. With alkaline salts they produce, as we have seen (394 and elsewhere), the acid anhydrides.

5th. With ammonia, or carbonate of ammonium, they give, as we shall learn hereafter, the primary amides.

6th. With the primary amides and the organic alkalies, they give, as we shall learn, the secondary amides and the alkalamides.

EXERCISES.

163. Write out the formulæ for the following bodies, and state how you would prepare them:—Chloride of butyryl, chloride of benzoyl, chloride of pelargyl, chloride of cinnamyl; chloride of capryl.

164. In how many volumes of these chlorides is one atom of chlorine contained?

DOUBLE MOLECULE.

H_2Cl_2.

POSITIVE CHLORIDES.

930. This group embraces—(1) The chlorides, &c., of the diatomic metals. (2) The chlorides, &c., of the di-

onium bases. (3) The chlorides of the radicals of the biatomic alcohols.

(1.) CHLORIDES OF THE POSITIVE METALS.

931. The metals which we have given under the double molecule of hydrogen are capable, of course, of forming chlorides, bromides, &c., on the type of a double molecule of chlorhydric acid (H_2Cl_2), thus:—

$$Pt''Cl_2;\ Pd''I_2;\ Sn''Cl_2.$$

932. The biatomic chlorides unite with monatomic chlorides, forming double salts. Example:—$K\,Cl,\ Pt\,Cl_2$.

(2.) CHLORIDES, ETC., OF DI-ONIUM BASES.*

933. As the preparation of these bodies is described in the polyammonia group, it is unnecessary here to enter upon the subject. We shall only give the student some exercises on these bodies.

EXERCISE.

165. State how you would prepare, and give the formulæ of, the following bodies:—Dibromide of ethylene diammonium, dibromide of hexethyl-ethylene diphosphonium, dibromide of triethylene diammonium, dibromide of ethylene triethyl-bimethyl phosphammonium, dibromide of diethylene-diethyl diammonium, dibromide of ethylene-triethyl arsammonium, dibromide of hexethyl-ethylene arsonium, dibromide of hexethyl-ethylene phospharsonium.

(3.) CHLORIDES OF THE BIATOMIC ALCOHOL RADICALS.

(*General formula*, $C_nH_{2n}Cl_2$.)

934. The members of the olefiant gas group combine readily, as we have already stated, with two equivalents of chlorine, of iodine, or of bromine, forming the bichlorides, biniodides, or the bibromides of these bodies.

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* This group of bases must not be attempted by the student until he has gone through the diamines and diamides. He then commences this; and when he has completed the exercises, he goes to the hydrated oxides of the di-oniums (par. 733).

EXERCISE.

166. The student must write out the formulæ of the following compounds:—Bibromide of butylene, bichloride of propylene, bichloride of amylene, bibromide of hexylene, bichloride of butylene.

935. *Preparation of these chlorides, iodides, and bromides.*—The direct action of chlorine, iodine, or bromine upon olefiant gas, or any other member of the series, gives respectively the bichloride, biniodide, or the bibromide of the member acted upon.

936. *Properties.*—These compounds are attacked by an alcoholic solution of potash. They are resolved by this agent into a chloride, bromide, or iodide of a radical, the general formula of which is $C_n H_{2n-1}$ (919), and hydrochloric, hydrobromic, or hydriodic acid. This property distinguishes them from the following compounds belonging to the haloid compounds of the monatomic alcohol radicals of the first class, viz., $C_2 H_4 Cl, Cl$; $C_2 H_4 Br, Br$; and $C_2 H_4 I, I$; for these latter bodies are not decomposed by an alcoholic solution of potash.

937. If, after these chlorine or bromine compounds have been obtained, we continue to act upon them with a further quantity of chlorine or bromine, we can replace one or more of the equivalents of hydrogen in the radical by its equivalent of chlorine or bromine. In the case of olefiant gas, all the hydrogen has been removed and replaced by chlorine. Example:—

		Boiling point, C.	Density.
1. Bichloride of ethylene (Dutch liquid) -	- $C_2 H_4 \quad Cl_2$	82·5	1·256
2. Bichloride of monchlor-ethylene -	- $C_2 H_3 Cl \quad Cl_2$	115	1·422
3. Bichloride of bichlor-ethylene -	- $C_2 H_2 Cl_2 \quad Cl_2$	135	1·576
4. Bichloride of trichlor-ethylene -	- $C_2 H \; Cl_3 \quad Cl_2$	153	1·610
5. Bichloride of quadrichlor-ethylene	- $C_2 Cl_4 \quad Cl_2$	180	2·000

938. The first four compounds, when treated with an alcoholic solution of potash, lose the elements of hydrochloric acid, and their formula then becomes,—

$$\begin{array}{l|l} C_2 H_3 Cl & C_2 H Cl_3 \\ C_2 H_2 Cl_2 & C_2 Cl_4 \end{array}$$

939. By the substitution of one atom of chlorine for one atom of hydrogen in the chlorides of the monatomic

alcohol radicals of the first class, we obtain bodies isomeric with the chlorides of these biatomic alcohol radicals. The two groups of bodies are distinguished from each other by their behaviour with an alcoholic solution of potash, as we have just noticed (936); but these monochlorinated chlorides of the *monatomic* alcohol radicals play the same part as the chlorides of the biatomic radicals. Monochlorinated chloride of ethyl, $(C_2H_4Cl)Cl$, for example, becomes transformed, like its *isomer*, bichloride of ethylene, $C_2H_4Cl_2$, into diacetate of glycol, by treating it with acetate of silver; it also fixes, like bichloride of ethylene, two molecules of ammonia, a diammonium chloride being formed, in which the C_2H_4 acts as a diatomic radical.

940. Dr. Maxwell Simpson has lately obtained cyanide of ethylene and cyanide of propylene. He prepared them by treating the bromides of these bodies with cyanide of potassium. A mixture of two equivalents of the cyanide, and one of the bromide, together with a considerable quantity of alcohol, was exposed, in well-corked soda-water bottles, to the temperature of a water-bath for sixteen hours. Subsequently the bottles were opened, and the alcohol separated by distillation. When purified, cyanide of ethylene, below the temperature of 37° C., is a crystalline solid of a light brown colour; above that temperature it is a fluid oil. Cyanide of propylene is a liquid at the ordinary temperature of the air. They are converted by potash, as we have already noticed, the one into succinic acid, and the other into pyrotartaric acid.

APPENDIX H.

APPENDIX TO THE GROUP.

941. When aldehyde is acted upon by pentachloride of phosphorus, an oily liquid is formed, which has the following formula, $C_2H_4Cl_2$; it is therefore *isomeric* with Dutch liquid, but it is distinguished from that body by its lower boiling point (60° C.) and specific gravity, and by its not being decomposed by an alcoholic solution of potash in the cold, and but slowly when heated. The C_2H_4 is therefore supposed to exist in this and other

compounds we shall notice, as a diatomic radical, and it has been called ethylidene. This radical is isomeric, but not identical with ethylene.

942. When the vapour of aldehyde is passed over pentabromide of phosphorus, in a vessel externally cooled, chemical action ensues, and the products formed are bibromide of ethylidene ($C_2H_4Br_2$), and oxybromide of phosphorus. The ethylidene compound cannot be separated from the phosphorus compound by fractional distillation, because the former compound is decomposed by heat; but the two compounds can be separated by agitating the mixture with lumps of ice, replacing them as they melt. A dense yellow liquid is thus obtained, which is insoluble in water, but is readily decomposed by it, with evolution of hydrobromic acid.

943. Oil of bitter almonds, and other aldehydes, yield also bichlorides of hydrocarbon radicals when treated with pentachloride of phosphorus. The composition and properties of these bodies we have already noticed in Appendix E, and par. 776.

944. Both bromine and iodine act upon allyl, the *one* forming bibromide of allyl, and the other biniodide of allyl. These bodies have not yet been sufficiently studied.

NEGATIVE OR ACID CHLORIDES.

945. This group embraces — (1) The hydrogen compounds of the biatomic radicals analogous to chlorine. (2) The chlorides of the biatomic radicals of the inorganic oxygen acids. (3) The chlorides of the biatomic radicals of the organic oxygen acids.

(1.) THE HYDROGEN COMPOUNDS OF THE BIBASIC RADICALS ANALOGOUS TO CHLORINE.

946. The radical in the ferrocyanides is biatomic; it may therefore be considered as representing the two equivalents of chlorine in the double molecule of hydrochloric acid. The formula of hydroferrocyanic acid, represented on this type, is $\{H_2[Fe(CN)_3]''\}$, and the general formula for the ferrocyanides $\{M_2[Fe(CN)_3]''\}$.

CHLORIDE OF BIATOMIC CYANOGEN.

$(CN)_2''\,Cl_2$.

(2.) CHLORIDES OF THE BIATOMIC RADICALS OF THE INORGANIC OXYGEN ACIDS.

Chloride of carbonyl, oxychloride of carbon, phosgene gas	CO'', Cl_2
Chloride of sulphuryl	$SO_2'' Cl_2$
Chloride of chromyl, or chlorochromic acid	Cr_2O_2'', Cl_2

(3.) CHLORIDES OF THE BIATOMIC RADICALS OF THE ORGANIC OXYGEN ACIDS.

947. *Preparation.*—These chlorides may be obtained by the action of pentachloride of phosphorus upon the corresponding anhydrous acid.

948. "The action of pentachloride of phosphorus on a bibasic acid, is supposed by Gerhardt to consist of two stages; the first being the formation of an anhydrous acid; the second, the conversion of that compound into a chloride. For example:—

$$\left.\begin{matrix} C_4H_4O_2.O \\ H_2.O \end{matrix}\right\} + PCl_3.Cl_2 = C_4H_4O_2.O + 2HCl + POCl_3;$$

and $C_4H_4O_2.O + PCl_3.Cl_2 = C_4H_4O_2.Cl_2 + POCl_3$;

whereas, in the case of a monobasic acid, the action consists of one stage only.

"This difference is connected by Gerhardt with the fact that a bibasic acid may be supposed to contain water, whereas a monobasic acid cannot (793). According to Williamson, on the contrary, the two stages of the reaction, in the case of a bibasic acid, are precisely similar to one another, and to the single reaction which takes place with monobasic acids. Thus, with sulphuric acid,—

$$\left.\begin{matrix} SO_2 \\ H_2 \end{matrix}\right\} O_2 + PCl_3.Cl_2 = \left.\begin{matrix} SO_2 \\ HCl \end{matrix}\right\} O + HCl + POCl_3;$$

$$\text{and } \left.\begin{matrix} SO_2 \\ HCl \end{matrix}\right\} O + PCl_3.Cl_2 = SO_2.Cl_2 + HCl + POCl_3.$$

The difference in the two views of the reaction is this,—that the former supposes the first stage of the action to consist in the formation of an anhydrous acid; the second supposes an intermediate compound—a chlorohydrate of the acid—to be produced. The formation of this chlorohydrate has been shown by Professor Williamson to take place with sulphuric acid. If, however, one of the two molecules of hydrochloric acid in Gerhardt's first equation be supposed to remain associated with the anhydrous acid, the two views will nearly coincide. In every case, indeed, the reaction consists essentially in the interchange of O and Cl_2."

EXERCISES.

167. Write out the formulæ for the following substances:—Ferrocyanide of potassium, bichloride of succinyl, ferrocyanide of potassium and barium.

168. How many volumes of these chlorides contain two atoms of chlorine?

TREBLE MOLECULE.

$H_3 Cl_3$.

POSITIVE CHLORIDES.

CHLORIDES OF THE POSITIVE METALS.

949. The ter and sesqui metals, which we have given under the treble molecule of hydrogen ($H_3 . H_3$), are capable, of course, of forming ter and sesqui chlorides, bromides, &c., thus:—

$$Au''' Cl_3 ;\ Ffe''' Cl_3$$

950. The teratomic chlorides, like the biatomic ones, unite with monatomic chlorides, forming double salts. Example:—$K Cl, Au''' Cl_3$.

CHLORIDES OF TRIATOMIC RADICALS.

951. We shall here notice the terchlorides of those radicals which are triatomic.

952. *Terbromide of allyl,* $C_3 H_5 Br_3$.—Obtained by gradually adding three parts of bromine to two parts of iodide of allyl, $C_3 H_5 I$, cooled in a freezing mixture, leaving the liquid to stand until the next day; then washing the liquid separated from crystallized iodine with alkaline, and afterwards with pure water; dehydrating; distilling (whereupon it turns brown, and gives off iodine vapours); again washing and distilling that which has passed over, collecting apart that which distils between 210° and 220°; cooling the purple-red liquid thus obtained

to 0°, whereupon it solidifies in the crystalline state; removing the red mother-liquor; and lastly, fusing and again rectifying the product.

953. It is a colourless, neutral liquid, having a not unpleasant odour; specific gravity 2·436 at 23° C.; solidifies below 10° (by slow cooling it yields shining prisms, which melt at 16°); boils between 217° and 218°. It is called isotribromhydrine by Berthelet and De Luca.

954. Terbromide of allyl is isomeric with terbromhydrine and bibromide of bromopropylene. It is distinguished from terbromhydrine, $C_3H_5Br_3$, by its boiling point. It is distinguished from bibromide of bromopropylene, $C_3H_5Br\,Br_2$, by its boiling point, its specific gravity, by solidifying above 0°, and by its behaviour with alcoholic potash, with ammonia, with oxide of silver, and with sodium. Terbromide of allyl is converted, by *alcoholic potash*, into an etherial liquid which boils at 135°. *Ammonia* converts it into bibromallylamine, $N(C_3H_4Br)_2H$, and bromide of ammonium. Bromide of bromopropylene, on the other hand, is converted by ammonia into bromide of ammonium, and a compound whose empirical formula is $C_6H_9Br_3$. With moist *oxide of silver*, terbromide of allyl yields bromide of silver and glycerine, whereas bromide of bromopropylene* does not yield glycerine when treated with silver salts. Terbromide of allyl is decomposed by sodium, yielding allyl and bromide of sodium; but it is difficult to remove the whole of the bromine. Bromide of bromopropylene, treated with sodium, yields, not allyl, but bibromopropylene, $C_3H_4Br_2$.

955. Terbromhydrine is obtained by acting upon bibromhydrine or epibromhydrine (bodies whose acquaintance the student made when studying the decompositions of glycerine) with pentabromide of phosphorus.

956. *Perchloride of vinyl or acetyl* ($C_2H_3Cl_3$).—"If chlorine gas is passed to saturation through chloride of ethylene, covered with a layer of water, and placed in a dark situation; the yellow liquid then brought into the light, where it loses its colour, becomes heated, and gives off hydrochloric acid, which dissolves in the water;

---

* This experiment ought to be repeated, varying the conditions, as the bromide of the bromopropylene ought by analogy to yield glycerine.

chlorine gas continuously passed through it for two days in the light; the watery stratum decanted, and the oil distilled, rejecting the first portion, which passes over below 115° C., and the last portion, which distils above 115° C. The portion obtained in the middle of the process at 115° C., and amounting to three-fourths of the whole, is a pure product."

957. Mixed with alcoholic potash, it immediately becomes heated, and forms a precipitate of chloride of potassium, and afterwards yields to distillation the liquid $C_2H_2Cl_2$, without any evolution of gas. Exposed to daylight in a bottle filled with chlorine, it is converted, in the course of twenty-four hours, into sesquichloride of carbon and hydrochloric acid,—

$$C_2H_3Cl_3 + 6\,Cl = C_2Cl_6 + 3\,HCl.$$

958. *Chloroform* ($CHCl_3$).—This substance is best prepared by distilling alcohol, wood spirit, or acetone, with a solution of chloride of lime. Bromoform, $CHBr_3$, and iodoform, CHI_3, are obtained in a similar manner. Hofmann has clearly proved, in his researches on the compound ammonias, that the radical, CH, in these bodies is triatomic.

NEGATIVE OR ACID CHLORIDES.

Chlorides of triatomic inorganic acids, or negative chlorides :—

Trichloride of bismuth - - - - -	$Bi''Cl_3$
Trichloride of antimony - - - - -	$Sb''Cl_3$
Trichloride of arsenic - - - - -	$As''Cl_3$
Trichloride of phosphorus - - - -	$P''Cl_3$
Trichloride of phosphoryl (oxychloride of phosphorus) - - - - - -	$(PO)''Cl_3$
Trichloride of sulphophosphoryl (sulphochloride of phosphorus) - -	$(PS)''Cl_3$

959. Antimony and phosphorus form also pentachlorides. These pentachlorides are sometimes viewed as the trichlorides of a compound chloride radical. Example :—

Chloride of chlorophosphoryl (pentachloride of phosphorus) - -	$(PCl_2)''Cl_3$
Chloride of triatomic cyanogen - -	$\left([(CN)_3]''Cl_3\right)$

The hydrogen compounds of the triatomic radicals, ferricyanogen and cobalticyanogen :—

$$\left(H_3[Fe_2(CN)_6]'''\right);\ \left(H_3[Co_2(CN)_6]'''\right).$$

These radicals, ferricyanogen and cobalticyanogen, are triatomic. They may be considered as replacing the three equivalents of chlorine in the treble molecule of hydrochloric acid. The general formula of their salts is therefore,—

$$\left(M_3[Fe_2(CN)_6]'''\right);\ \left(M_3[Co_2(CN)_6]'''\right).$$

QUADRUPLE MOLECULE.

$$H_4Cl_4.$$

POSITIVE CHLORIDES.

THE CHLORIDES OF THE POSITIVE METALS.

960. Tin and titanium form chlorides on the type of the quadruple atom; the following are therefore the symbols of the molecules of these chlorides, $Sn''''\,Cl_4$; $Ti''''\,Cl_4$.

NEGATIVE GROUP.

Chlorides of tetratomic elements.

Tetrachloride of carbon - - -	$C''''\,Cl_4$
Tetrachloride of silicon - - -	$Si''''\,Cl_4$

961. "Each tetrachloride has a corresponding bichloride, and the general behaviour of the tetrachlorides shows that two of the chlorine atoms are held less forcibly than are the other two."

CHAPTER X.

AMMONIA TYPE.

962. Ammonia, chloride of ammonium, and hydrated oxide of ammonium, although they are all members of the ammonia family, are, nevertheless, constructed on different types. Ammonia, $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$, is the prototype of a

large class of bodies; chloride of ammonium, NH_4Cl, is constructed on the type of hydrochloric acid; and hydrated oxide of ammonium, $\left.\begin{matrix}H_4N\\H\end{matrix}\right\}O$, is constructed on the type of water. One, or even all the atoms of hydrogen in ammonia, in chloride of ammonium, and the atoms in the ammonium in hydrated oxide of ammonium, can be replaced by an equivalent number of simple or compound radicals; these derivatives belong, of course, to the same type as the ammonia, the chloride of ammonium, or the hydrated oxide of ammonium, from which they are derived.

963. Phosphoretted hydrogen, $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}P$, arsenetted hydrogen, $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}As$, and antimonetted hydrogen, $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}Sb$, are constructed on the ammonia type; the hydrogen in these bodies can be replaced, as the hydrogen in the prototype, by other radicals. These derived bodies belong, of course, to the same type, ammonia, as the bodies from which they are derived. Bodies containing phosphorus, antimony, and arsenic, have been produced, resembling chloride of ammonium and hydrated oxide of ammonium in their constitution; these, therefore, necessarily belong to the hydrochloric acid type and the water type, respectively.

964. By means of polyatomic radicals, two, three, four, or even five atoms of ammonia or phosphide, arsenide or antimonide, of hydrogen, can be made to coalesce, the polyatomic radical replacing its equivalent number of hydrogen atoms in the ammonia, &c. We can, in this way, even bind together ammonia with its phosphoretted, antimonetted, or arsenetted analogue.

965. There are, therefore, mon-ammonias and poly-ammonias, and mon-ammoniums and poly-ammoniums. The mon and poly-ammonias are constructed on the type of one, two, or more, atoms of ammonia; they will, therefore, be considered under this type. The mon and poly-*oniums* come under the type hydrochloric acid, or the type water; if the *onium* body is combined with any of the halogen elements, or with cyanogen, it comes under the type hydrochloric acid; the other onium compounds come under the type water.

966. We shall now specially consider the bodies which are constructed on the type of a single molecule of ammonia.

Simple Molecule.

$$\left.\begin{array}{l}H\\H\\H\end{array}\right\}N$$

967. This group embraces—(1) Monamines. (2) The phosphines, arsines, and stibines. (3) The metalamides. (4) The organo-amides.

968. The derivatives of ammonia can be formed by replacing the hydrogen of the ammonia either by *alcohol radicals*, or by *acid radicals*, or by *metals*. When it is replaced by the alcohol radicals, the basic character of the ammonia is more or less preserved; but when it is replaced by the acid radicals, it is lost; but there is such a gradual transition from one group to the other, as regards whether they can, or cannot, combine with acids, that it is frequently difficult to decide from this test to which class an ammonia derivative belongs. But the bodies belonging to the basic class do not yield up, when boiled with potash, ammonia and the radicals whose introduction into ammonia has produced them; indeed, hitherto, very few processes are known in which these bodies yield up their radicals. The bodies belonging to the neutral class, on the other hand, are readily decomposed into ammonia and the hydrated oxides of their radicals. The simplest manner, therefore, of distinguishing to which class any ammonia derivative belongs, consists in boiling the compound under examination with potash;—if it belongs to the basic class, it will remain unaltered; if it belongs to the neutral class, ammonia will be evolved, and a potassium salt formed.

969. The bodies belonging to the basic class are designated by the general terms—amines, phosphines, arsines, stibines,—according as they contain nitrogen, phosphorus, arsenic, or antimony.

970. The bodies in which the basic character is extinct are distinguished by the termination *ide*, as amides, &c.

971. The amine class embraces that large number of compounds known as organic bases, many of which are

elaborated in animals and plants (animal and vegetable alkaloids), whilst the greater number are produced in the laboratory (artificial bases). The bodies composing the amide class are mostly produced by artificial processes, comparatively few terms of this group having been met with in the animal or vegetable organism. Both the amines and amides are divided into mon, di, tri, and tetra compounds, according as they are derived from one, two, thee, or four molecules of ammonia. We have, therefore,—

Amines.	Amides.
Monamines	Monamides
Diamines	Diamides
Triamines	Triamides
Tetramines	Tetramides

(1.) MONAMINES.

972. By this term we designate a very numerous class of bodies derived from one molecule of ammonia,—bodies in which the basic character of this substance—its power of combining with acids—is preserved. Some of these bodies are found in nature; but the majority have been obtained by artificial processes, some of which are of very general applicability, and admit of producing an almost unlimited number and variety of this class of substances. The monamines may be again classed into three subdivisions, according to the number of hydrogen equivalents in the ammonia molecule which are replaced. We distinguish—1st. *Primary monamines*, sometimes called amidogen bases; derived from one molecule of ammonia by the substitution of a radical for one equivalent of hydrogen. 2nd. *Secondary monamines*, sometimes called imidogen bases; formed by the substitution of radicals for two equivalents of hydrogen. 3rd. *Tertiary monamines*, sometimes called nitrile bases; formed by the substitution of radicals for the three equivalents of hydrogen. These three subdivisions may be represented by the following general formulæ:—

Primary monamines. (Amidogen bases.)	Secondary monamines. (Imidogen bases.)	Tertiary monamines. (Nitrile bases.)
$\left.\begin{matrix}A\\H\\H\end{matrix}\right\}N$	$\left.\begin{matrix}A\\B\\H\end{matrix}\right\}N$	$\left.\begin{matrix}A\\B\\C\end{matrix}\right\}$

EXAMPLES.

Phenylamine (Aniline).	Dimethylamine.	Methyl-ethyl-amylamine.
$\left.\begin{matrix}(C_6H_5)\\ H\\ H\end{matrix}\right\}N$	$\left.\begin{matrix}CH_3\\ CH_3\\ H\end{matrix}\right\}N$	$\left.\begin{matrix}CH_3\\ C_2H_5\\ C_5H_{11}\end{matrix}\right\}N$

Two or even the three atoms of hydrogen can be replaced by two or three equivalents of one monatomic radical, or, as shown by methyl-ethyl-amylamine, each equivalent of hydrogen may be replaced by a different radical.

PRIMARY MONAMINES.

973. *Preparation.*—1st. We have already seen (410) that these bodies are formed by the action of potash on the cyanates or cyanurates.

2nd. They are also formed,—and this is the way they are generally prepared,—by the action of the bromides or iodides of the alcohol radicals upon ammonia, thus:—

$$C_2H_5I + NH_3 = (C_2H_5)H_3N, I;$$

an haloid compound being formed. In the example we have selected, iodide of ethyl-ammonium is formed. The ammonium compound thus formed, when treated with potash, is decomposed into the corresponding primary monamine and hydriodic acid:—

$$(C_2H_5)H_3N, I + \left.\begin{matrix}K\\ H\end{matrix}\right\}O = \left.\begin{matrix}C_2H_5\\ H\\ H\end{matrix}\right\}N + KI + \left.\begin{matrix}H\\ H\end{matrix}\right\}O$$

3rd. We have already noticed that one, two, or even more atoms of hydrogen in the hydrides of the third class of alcohol radicals, and in other bodies, can be replaced by NO_2. If the mono-nitro compounds of these bodies are submitted to the action of reducing agents, such as hydrosulphuric acid or nascent hydrogen, the two atoms of oxygen are removed, and two atoms of hydrogen are substituted for them, and the compound produced by the substitution is an organic base. Example:—

$$C_6H_5NO_2 + 3\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}S\right) = \left.\begin{matrix}C_6H_5\\ H\\ H\end{matrix}\right\}N + 2\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right) + 3S.^*$$

When two or three atoms of hydrogen in the hydride are replaced by two or three atoms of NO_2, it is more difficult to reduce the second or third atom of NO_2 by H than the first; we can, therefore, have one or two atoms of NO_2, replacing one or two atoms of H in the organic base as well as in the hydride; but the basic properties of the base become weakened by this substitution. Example:—

---

* See Appendix I., page 414.

Nitrophenylamine,

$$\left.\begin{matrix}(C_6H_4, NO_2)\\ H\\ H\end{matrix}\right\} N.$$

When the second atom of NO_2 is reduced, a diamine is produced, as we shall learn hereafter.

4th. The primary, secondary, and tertiary monamines are frequently produced in the destructive distillation of nitrogenized organic substances; they are therefore found in such substances as coal tar, bone oil, &c. They are also formed in the putrefaction and fermentation of nitrogenized organic bodies.

974. The hydrogen in the radicals can be partly replaced, we have seen, by NO_2. It can also be partly replaced by chlorine, bromine, or iodine; but the basic character is impaired by the substitution.

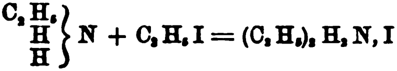
EXERCISES.

169. Give the formula for ethylamine, for amylamine, for allylamine, for tolylamine; and state the different methods by which they could be prepared.

170. Give the formula for chlorphenylamine, for dinitrophenylamine, for dichlorphenylamine, and for trichlorphenylamine, for bromaniline, for bibromaniline, for tribromaniline.

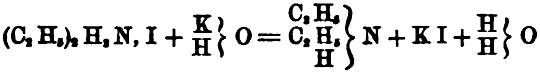
SECONDARY MONAMINES.

975. *Preparation.*—When the primary monamines are treated with the bromides or iodides of the alcohol radicals, we obtain the iodide or bromide of a secondary monammonium. Example:—



$$\left.\begin{matrix}C_2H_5\\ H\\ H\end{matrix}\right\} N + C_2H_5I = (C_2H_5)_2 H_2 N, I$$

These bromides or iodides of secondary monammoniums, when treated with potash, are decomposed into the corresponding secondary monamine and hydriodic or hydrobromic acids. Example:—



$$(C_2H_5)_2H_2N,I + \left.\begin{matrix}K\\H\end{matrix}\right\}O = \left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}N + KI + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

976. Two natural alkalies belong to this class. The nature of the radicals which occupy the place of the two equivalents of hydrogen is unknown; we do not even know whether the radicals are monatomic or diatomic. The alkalies are—

Piperidine - - $C_5H_{11}N = (C_5H_{10})HN$
Conine - - - $C_8H_{15}N = (C_8H_{14})HN$

EXERCISE.

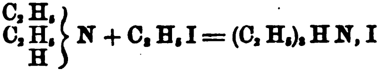
171. Give the formula for dimethylamine, for diamylamine, for ethyl-phenylamine, for ethyl-tolylamine; and state the different methods by which they could be prepared.

TERTIARY MONAMINES.

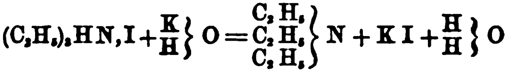
977. *Preparation.*—1st. A primary monamine can be converted into a secondary, and a secondary can be converted into a tertiary, by acting upon it with chloride or bromide of cyanogen.

2nd. We have seen that if we act upon the cyanates of the alcohols by potash, we obtain primary monamines. If, in place of potassium, we use potassium alcohols,—bodies in which the hydrogen in hydrate of potash is replaced by an alcohol radical,—we obtain tertiary monamines.

3rd. If we act upon a secondary monamine with a bromide or iodide of an alcohol radical, we obtain the iodide or bromide of a tertiary monammonium. This is decomposed by potash into the corresponding tertiary monamine and hydriodic acid. Example:—

(1.)


$$\left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}N + C_2H_5I = (C_2H_5)_3HN,I$$

(2.)


$$(C_2H_5)_3HN,I + \left.\begin{matrix}K\\H\end{matrix}\right\}O = \left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}N + KI + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

978. When a bromide of an alcohol radical is employed to act upon ammonia, it appears to act in the gradual manner we have just indicated, viz., the bromide

of the primary monammonium is formed. This, when decomposed by potash, yields the primary monamine; this, when again acted upon by the bromide, yields the bromide of the secondary monammonium; this, when acted upon by potash, yields the secondary monamine, &c. When the bromide of the triammonium has been produced $(C_x H_y)_3 H Br$, continued digestion with the bromide of the radical fails to replace, or at least replaces very slowly, the last atom of hydrogen, so as to form the bromide of the tetrammonium; but if we substitute iodide of ethyl, or iodide of methyl, especially the latter, for the bromide, the hydrogen atom is instantly replaced.

979. If, however, we employ the iodides instead of the bromides, the substitution does not go forward in that transitional manner we have indicated, on account of the iodide being more readily decomposed. As, therefore, the first substitution product, the iodide of the monammonium, is generated in the presence of the easily-decomposed substitution agent, it is immediately acted upon by it, the second substitution product being formed, which becomes in the same way converted into the third, and this into the fourth; so that all the four bases are simultaneously formed, but by no means in equal quantities. When iodide of methyl is used as the substitution agent, all the four iodides are formed, but the first and last terms of the series are formed in the largest quantities. When iodide of ethyl is employed, the substitution is more gradual; iodide of monethylammonium is always formed, but the other three, especially iodide of diethylammonium, are always formed in very appreciable proportions. The simultaneous formation of all the four bases has presented a difficulty which has greatly interfered with the general application of this otherwise convenient method; but Hofmann has lately proposed a simple and elegant method for the separation of the three amines, which we elsewhere give (Appendix K). We must now draw the student's attention to the different deportment the iodide of the tetra compounds displays with potash, to what the *ter*, *di*, and *mon* display. We have seen that the three latter are decomposed by that reagent with formation of hydriodic acid, and the corresponding amine; but it is not so with the tetra compounds. These iodides are unacted upon by potash; but if we digest the iodides with freshly-precipitated oxide of

silver, iodide of silver and the hydrate of the tetrammonium body are formed. The hydrates of the tetrammoniums are decomposed by distillation into the tertiary monamines, and other products, which we shall not now notice; the tertiary monamines are therefore obtained by the distillation of the hydrates of the tetrammoniums.

980. To this group, tertiary monamines, belong the artificial sulphuretted bases obtained by the action of sulphuretted hydrogen upon the combination of ammonia and the aldehydes (489).

981. To this group belongs also a number of vegetal alkalies, of which nicotine $(C_5H_7)'''N$, morphine $(C_{17}H_{19}O_3)'''N$, and codeine $(C_{18}H_{21}O_3)'''N$, are prominent terms. A considerable number of bases produced in the distillation of coal, of animal matters, and of nitrogenized bodies in general, are tertiary monamines.

Pyridine	$(C_5H_5)'''N$
Picoline	$(C_6H_7)'''N$
Lutidine	$(C_7H_9)'''N$
Leucoline	$(C_9H_7)'''N$
Lepidine	$(C_{10}H_9)'''N$

982. "All the members belonging to the three groups, viz., primary, secondary, and tertiary monamines, are true ammonias. They combine with the hydrogen acids, with the so-called hydrated oxygen acids, without elimination of water, forming saline bodies, generally of well-defined character. Their hydrochlorates yield, with bichloride of platinum, with terchloride of gold, with chloride of mercury, and many other chlorides, a series of very characteristic salts, which have often been studied with a view of fixing the nature of the organic constituent. Nearly all the monamines are volatile, their boiling points being lower or higher, according to the number of hydrogen equivalents replaced, and according to the nature of the compound molecules by which the substitution is effected. Nearly all these bodies are characterised by a peculiar odour, frequently resembling the odour of ammonia, but likewise considerably modified by the degree and nature of the substitution. Most of these bodies, when in contact with water, exhibit the alkaline reaction of ammonia, which is, however, considerably diminished in some, and altogether lost in others."

983. Whether an organic base is a primary, secondary, or tertiary mónamine, is established by ascertaining whether a substitution of hydrogen takes place on treating it with the iodide of methyl or ethyl. If three atoms of the alcohol radical unite with the base, it is a primary monamine; if two atoms of the alcohol radicals are fixed by the base, then it is a secondary monamine; but if only one atom of the alcohol radical is fixed, the base is a tertiary monamine. A base corresponding to hydrated oxide of ammonium does not fix an atom of the alcohol radical. We cannot, however, learn by this test what is the atomic saturation of the organic radicals contained in the base. For example, the empirical formula of the base conine, which exists in the plant *Conium maculatum*, is $C_8 H_{15} N$. Now as we can replace one atom of hydrogen in this compound by an alcohol radical, we learn from this reaction that conine is a secondary monamine; therefore $C_8 H_{14}$ occupies the place of two atoms of hydrogen; but whether this $C_8 H_{14}$ is a diatomic radical, or it is two atoms of a monatomic radical, $C_4 H_7$, or two atoms of two different monatomic radicals, we do not know; no method is at present known which enables us to solve this problem.

EXERCISES.

172. How many atoms of ethyl or methyl would aniline fix? Express the reaction between the iodide and the base, by an equation.

173. Write out the formula for cyandiethylamine, for methy-ethyl-phenylamine, for diethyl-tolylamine, for trimethylamine, for triethylamine, for triamylamine; and state the different methods by which they could be prepared.

174. Among the ammonia derivatives which exist in the brine of salt herrings, is one the empirical formula of which is $C_3 H_9 N$. The chemist who first obtained this base from herring brine concluded that it was a primary monamine,—that it was, in fact, propylamine,

$$\left.\begin{matrix} C_3 H_7 \\ H \\ H \end{matrix}\right\} N.$$

It was afterwards ascertained that it was a tertiary monamine, trimethylamine,

$$\left.\begin{matrix} C H_3 \\ C H_3 \\ C H_3 \end{matrix}\right\} N.$$

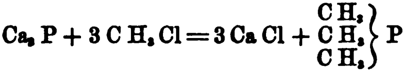
How can it be ascertained to which of the three groups of monamines this or any amine belongs; or whether it is an amine or an ammonium derivative?

175. What would be produced if two equivalents of aniline and one equivalent of bromide of ethyl were added together?

(2.) THE PHOSPHINES, ETC.

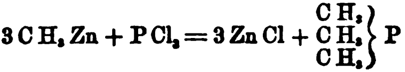
984. The phosphines, the arsines, and the stibines, have not yet been formed by direct substitution from their hydrogen compounds; and as yet only the tertiary compounds have been formed.

985. *Preparation.* 1st method.—They can be obtained by acting upon the metallic compounds of phosphorus, arsenic, and antimony, with the chlorides, bromides, or iodides of the alcohol radicals. Example:—



$$Ca_3 P + 3\,CH_3Cl = 3\,CaCl + \left.\begin{array}{l} CH_3 \\ CH_3 \\ CH_3 \end{array}\right\} P$$

2nd method.—They can also be prepared by acting upon their chlorides with the metallic combinations of the alcohol radicals. "This method furnishes the substances in greater abundance, and of remarkable purity."



$$3\,CH_3Zn + PCl_3 = 3\,ZnCl + \left.\begin{array}{l} CH_3 \\ CH_3 \\ CH_3 \end{array}\right\} P$$

986. The arsines and stibines, unlike the amines, do not unite with acids. The phosphines, on the other hand, resemble the amines in this respect, as they combine with hydrochloric acid, with sulphuric acid, &c., forming compounds on the ammonium type, thus:—

$$(CH_3)_3P + HCl = (CH_3)_3HP, Cl$$

987. The phosphines, arsines, and stibines, but not the amines, combine directly with oxygen, chlorine, sulphur, &c., forming saline bodies, the composition of which we will illustrate by the stibine compounds $(C_2H_5)_3SbO$, $(C_2H_5)_3SbCl_2$, $(C_2H_5)_3SbS$.

988. This difference in chemical properties between the derivative compounds of nitrogen and the corresponding derivative compounds of arsenic and antimony,

we find also in their hydrides; and in this class of compounds we find that the phosphorous body holds an intermediate position. Ammonia combines with acids; antimonetted and arsenetted hydrogen do not: phosphoretted hydrogen has been combined with a few acids, but its basic powers are very feeble; but when the derivatives are converted into bodies analogous to hydrated oxide of ammonium, this gradation in properties ceases: in the *onium* bodies, analogy of composition induces an almost absolute identity of chemical deportment.*

EXERCISE.

176. Write out the formula for triethyl-phosphine, for trimethyl-stibine, and triethyl-arsine.

APPENDIX I.

989. The nitro compounds may be reduced in a variety of ways,—by sulphuretted hydrogen, by the action of nascent hydrogen, by protosalts of iron: these are the most important. We shall give a description of these methods when employed on the large scale for the transformation of nitrobenzole into aniline.

1. *By means of sulphide of ammonium.*—An alcoholic solution of nitrobenzole, after having been saturated with ammoniacal gas, is treated with a current of sulphuretted hydrogen. The liquor now becomes of a deep, dirty-green colour, and deposits a little sulphur. It is now left for twenty-four hours, during which time crystals of sulphur are deposited, the odour of sulphuretted hydrogen

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* When bisulphide of carbon and triethyl-phosphine are brought together in the anhydrous condition, they combine with explosive violence, a deep *crimson-coloured crystalline* compound being produced. The substance is obtained in better crystals if etherial solutions, instead of the anhydrous compound, be employed. The new body separates in beautiful crimson leaflets the moment the two solutions are mixed together. Bisulphide of carbon and triethyl-phosphine become, on account of this reaction, most delicate tests for one another. Dr. Hofmann has employed triethyl-phosphine for the detection of bisulphide of carbon in coal gas. For this purpose he places an etherial solution of triethyl-phosphine in a bulb apparatus, and then passes a current of coal-gas through. Ruby crystals are formed if the sulphur compound is present.

disappears, and is replaced by a strongly ammoniacal smell. If distilled now to recover the alcohol, a good deal of sulphur is deposited, and it is impossible to continue the distillation long, because of the violent bumping which ensues; it is therefore allowed to cool, and the sulphur is removed. The process must be continued, re-saturating the liquor with sulphuretted hydrogen, if need be, until a heavy oily matter (aniline) deposits, which must be separated from the liquor, and re-distilled by itself. The aniline is thus obtained nearly pure.

Instead of using an alcoholic solution of nitrobenzole, and treating it successively with ammonia and sulphuretted hydrogen, the alcoholic solution of sulphide of ammonium may be prepared beforehand, and the nitrobenzole poured into it. A part is dissolved immediately, and the remainder by degrees in the course of the operation. It is sometimes advantageous, instead of waiting until the aniline separates, to add hydrochloric acid to the liquor in the retort, until it is slightly acid, and then to distil almost to dryness, by which means chloride of aniline is obtained. This is decomposed by an excess of caustic soda, and the aniline set at liberty is distilled off.

To avoid any danger from the bumping, a tinned copper still must be used, which should be heated by steam, under a slight pressure. At first the temperature should not exceed 90° C., but after some time it may be raised to 100° or 110°.

The ammoniacal alcohol condensed in the worm may be re-saturated with sulphuretted hydrogen, and used over again, with a new quantity of the nitrobenzole.

2. *Reduction of the nitrobenzole by nascent hydrogen.*—In preparing aniline by this process, the nitrobenzole and zinc are placed in a vessel, and dilute sulphuric or hydrochloric acid is added, so as to produce the disengagement of a small quantity of hydrogen. By degrees the nitrobenzole disappears, and aniline is formed, which remains in solution in the hydrochloric or sulphuric acid. To isolate it an excess of caustic soda is added, and the mixture is distilled, on which the aniline passes over with the vapour of water.

3. *Reduction of nitrobenzole by means of arsenite of potash or soda.*—Wholer, who invented this process,

digests nitrobenzole with a solution of arsenious acid in a strong lye of caustic soda; places the arsenical solution in a tubulated retort, heats it to the boiling point, and then allows the nitrobenzole to fall in, drop by drop. Under these circumstances, nitrobenzole is transformed into aniline, which distils over; and it is only necessary to saturate with an alcoholic solution of oxalic acid to obtain perfectly pure oxalate of aniline.

4. *Reduction by protosalts of iron.*—Sulphate, oxalate, and protochloride of iron have no sensible action upon these nitro compounds; but an iron salt, with a weak acid, the protoacetate, for example, is quickly acted upon. No gas is evolved. Sesquioxide of iron is precipitated, partly in the state of basic acetate, and the organic base is formed. Béchamp was the discoverer of this method of forming the artificial organic bases from the nitrocompounds. To prepare aniline by this method, nitrobenzole is poured into a solution of protoacetate of iron; the latter is almost immediately reduced, an evident sign of the oxidation of the protoxide of iron. If the vessel containing the mixture be placed in a bath heated to 212° F., a yellow ochreous deposit is soon formed, and no gas is evolved. If the solution of acetate of iron contains twelve equivalents of that metal to every equivalent of nitrobenzole, the aromatic odour of the nitrated compound disappears, and gives place to the peculiar odour of acetate of aniline. The following is the reaction which takes place:—

$$C_6H_5NO_2 + 6\left(\left.\begin{matrix}Fe\\Fe\end{matrix}\right\}O\right) + \left.\begin{matrix}H\\H\end{matrix}\right\}O = C_6H_7N + 3\left(\left.\begin{matrix}Fe_2\\Fe_2\end{matrix}\right\}O_3\right)$$

As this process is not so advantageous as the following, we shall not describe it further.

Béchamp ascertained that by distilling a mixture of nitrobenzole, iron filings, and acetic acid, aniline is formed, in accordance with the following equation:—

$$C_6H_5NO_2 + \left.\begin{matrix}H\\H\end{matrix}\right\}O + 4\,Fe = \left.\begin{matrix}Fe_2\\Fe_2\end{matrix}\right\}O_3 + C_6H_7N$$

He places in a large retort 1 part of nitrobenzole, 1·2 parts of bright iron filings, and 1 part of concentrated commercial acetic acid, free from mineral acid. The quantity of acetic acid should be sufficient to cover the iron filings completely. The reaction soon commences, without the aid of heat; it becomes exceedingly brisk, the temperature rises, the liquid begins to boil, and all will be lost if the receiver be not well cooled. The results of the reaction are, aniline, acetate of aniline, and a little nitrobenzole, which escapes the reaction. When the retort is cooled, the contents of the receiver are poured into it. Heat is then applied to the apparatus, and the whole is distilled to dryness. An excess of a solution of caustic potash is added to the distillate, when the hydrated aniline separates and rises to the surface, and may be removed and dehydrated in the usual manner.

The residue of the mixture of iron filings, acetic acid, and nitrobenzole, which remains in the retort after the distillation, still contains a considerable amount of aniline. To obtain this, the retort must be washed out with water acidulated with sulphuric or hydrochloric acid, the solution filtered, and then evaporated to dryness. The dry residue is then mixed with quicklime, and placed in a retort of iron or refractory ware, and distilled; the aniline thus obtained must be rectified.*

APPENDIX K.

990. *Separation of the three ethyl-ammonias.*—Although the differences between the boiling points of the three ammonias is considerable,—

	Boiling point.
Ethylamine - - - -	18° C
Diethylamine - - - -	57·5°
Triethylamine - - - -	91°

they cannot be separated by fractional distillation. Hofmann found that even after ten fractional distillations the bases were far from being pure.

Hofmann has lately discovered a simple and elegant process by which the three ethyl bases may be easily and perfectly separated. This process consists in submitting the *anhydrous* mixture of the three bases to the action of anhydrous oxalate of ethyl. By this treatment, ethylamine is converted into diethyl-*oxamide*, a beautifully crystalline body, very difficultly soluble in water; diethylamine into *diethyl-oxamate of ethyl*, a liquid boiling at a very high temperature; whilst triethylamine is not affected by oxalic ether.

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* Kopp "On the Preparation of Artificial Colouring Matters."— *Chemical News*, vol. ii. And Béchamp "On the Action of Protosalts of Iron on Nitronaphthaline and Nitrobenzole."—*Chemical Gazette*, vol. xiii., 1855.

By the action of oxalic ether upon ethylamine, two substances may be formed, viz., *ethyloxamate of ethyl*, and *diethyloxamide*.

Oxalic ether. Ethyloxamate of ethyl.

$$(1)\quad \left.\begin{matrix}(C_2O_2)''\\(C_2H_5)_2\end{matrix}\right\}O_2 + \left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N = \left[\left.\begin{matrix}(C_2O_2)''(C_2H_5)\,H\,N\\C_2H_5\end{matrix}\right\}O\right] + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$$

Diethyloxamide.

$$(2)\quad \left.\begin{matrix}(C_2O_2)''\\(C_2H_5)_2\end{matrix}\right\}O_2 + 2\left[\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N\right] = \left.\begin{matrix}(C_2O_2)''\\(C_2H_5)_2\\H_2\end{matrix}\right\}N_2 + 2\left[\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O\right]$$

In practice it appears that the second of these compounds only is produced. In the action of oxalate of ethyl upon diethylamine, two similar phases may be distinguished, capable of producing, respectively,—

(1) Diethyloxamate of ethyl, $\left[\left.\begin{matrix}(C_2O_2)''\,(C_2H_5)_2N\\C_2H_5\end{matrix}\right\}O\right]$, and

(2) Tetrethyloxamide - - - $\left.\begin{matrix}(C_2O_2)''\\(C_2H_5)_2\\(C_2H_5)_2\end{matrix}\right\}N_2$

In practice the *first* of these two compounds only is generated.

The action of oxalate of ethyl upon triethylamine might have involved the formation of the secondary oxalate of tetrethylammonium.

$$\left.\begin{matrix}(C_2O_2)\\(C_2H_5)_2\end{matrix}\right\}O_2 + 2\left[\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}N\right] = \left.\begin{matrix}(C_2O_2)''\\{[(C_2H_5)_4N]_2}\end{matrix}\right\}O_2:$$

under the circumstances under which I have worked, the two substances do not combine.

The product of the reaction of oxalate of ethyl upon the mixture of the ethyl bases, when distilled in the water-bath, yields *triethylamine* free from *ethylamine* and *diethylamine*.

The residue in the retort solidifies, on cooling, into a fibrous mass of crystals of diethyloxamide, which are soaked with an oily liquid. They are drained from the oil and recrystallized from boiling water. Distilled with potassa, these crystals furnish ethylamine free from *diethylamine* and *triethylamine*.

The oily liquid is cooled to 0°C., when a few more of the crystals are deposited; it is then submitted to distillation. The boiling point rapidly rises to 260°. What distils at that temperature is pure diethyloxamate of ethyl, from which, by distillation with potassa, *diethylamine, free from ethylamine and triethylamine*, may be obtained.[*]

Since the time that Dr. Hofmann communicated the above report to the Royal Society, on the separation of the three bases, he has added the following as a note to another paper:—"The separation of the ethyl-bases has been since repeatedly carried out. The process, as described in the 'Proceedings,' admits of a slight improvement. I proposed to separate the mixture of diethyloxamide and diethyloxamate of ethyl by filtration, and to purify the former by recrystallization from boiling water, the latter by exposure to a temperature of 0°. The separation is simpler and more perfect by submitting the mixture at once to the action of boiling water, when diethyloxamide dissolves, the diethyloxamate of ethyl remaining as an insoluble layer floating upon the hot solution, from which it may be separated by a tap-funnel."[†] This method can also be adopted for the separation of the methyl-ammonias. (See "Compt-Rendus," tom. lv., 1862, page 749).

AMIDES.

991. "By this term chemists have designated a very large class of substances derived from ammonia by substituting, for the hydrogen, acid radicals whose presence destroys the fundamental character of ammonia, viz., its power of combining with acids. The amides have

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[*] Dr. Hofmann "On the Separation of the Ethyl-Bases."—*Proceedings of the Royal Society*, vol. xi., No. 42.

[†] "Action of Chloracetic Ether on Triethylamine and Triethylphosphine," by Dr. Hofmann.—*Proceedings of the Royal Society*, vol. xi., No. 43.

been often defined as neutral derivatives of ammonia, similar in constitution to the amines; but the division of the ammonia-derivatives into *amines* and *amides*, is essentially artificial; there is, in fact, a gradual transition from one group to the other, and frequently we meet with substances, the position of which in the system is uncertain. The saline compounds of many amines are so extremely weak that they are decomposed by mere contact with water. On the other hand, recent researches have proved that in several substances long considered as well-established amides, the basic character of the mother-compound is far from being extinct, and that, under special circumstances, combinations with acids may be formed, in many respects analogous to the ammonium-salts, but of comparatively little stability. A much more characteristic mark of distinction between the amines and amides is furnished in the deportment of the two classes under the influence of decomposing agents. As yet very few processes are known in which the amines yield up, in any form, the radicals whose introduction into ammonia has produced them. The amides, on the other hand, are readily decomposed into ammonia and the hydrated oxides of their radicals. The simplest manner of distinguishing an *amine* from an *amide*, consists in boiling the compound under examination with potash, when the *amine* remains unaltered, the *amide* evolving ammonia with formation of a potassium salt.

992. "With very few exceptions, the amides are artificial compounds. Some of the processes which give rise to their formation are of very general applicability, so as to admit of the production of an almost unlimited number and variety of these substances."

MONAMIDES.

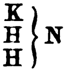
993. The amides derived from one molecule of ammonia are designated by this term; they are subdivided, like the monamines, into three classes, according to the number of the hydrogen equivalents of ammonia which are replaced, thus:—

Primary monamides.	Secondary monamides.	Tertiary monamides.
$\left.\begin{matrix}A\\ \mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{N}$	$\left.\begin{matrix}A\\ B\\ \mathrm{H}\end{matrix}\right\}\mathrm{N}$	$\left.\begin{matrix}A\\ B\\ C\end{matrix}\right\}\mathrm{N}$

(3.) METALAMIDES.

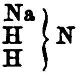
994. Comparatively few metalamides are at present known; and, as yet, only primary and tertiary ones are known.

Potassamide.



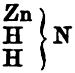
$$\left.\begin{array}{l}K\\H\\H\end{array}\right\}N$$

Sodamide.



$$\left.\begin{array}{l}Na\\H\\H\end{array}\right\}N$$

Zincamide.



$$\left.\begin{array}{l}Zn\\H\\H\end{array}\right\}N$$

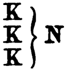
Potassamide and sodamide are formed by passing a current of dry ammonia over potassium and sodium, hydrogen being liberated, thus:—

$$H_3N + K = KH_2N + H$$

Zincamide is formed by acting upon zinc-ethyl with ammonia, hydride of ethyl being the ethyl compound which is produced, thus:—

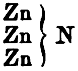
$$H_3N + ZnC_2H_5 = ZnH_2N + C_2H_5H$$

Tripotassamide.



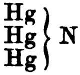
$$\left.\begin{array}{l}K\\K\\K\end{array}\right\}N$$

Trizincamide.



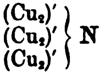
$$\left.\begin{array}{l}Zn\\Zn\\Zn\end{array}\right\}N$$

Trimercuramide.



$$\left.\begin{array}{l}Hg\\Hg\\Hg\end{array}\right\}N$$

Tricuprosamide.



$$\left.\begin{array}{l}(Cu_2)'\\(Cu_2)'\\(Cu_2)'\end{array}\right\}N$$

Tripotassamide and trizincamide are formed by the action of heat upon the primary amides of these metals, ammonia being generated, thus:—

$$3KH_2N = K_3N + 2H_3N$$

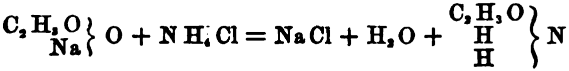
Trimercuramide and tricuprosamide are obtained by submitting the metallic oxides to the action of ammonia, thus:—

$$2H_3N + 3Hg_2O = 2Hg_3N + 3H_2O.$$

(4.) ORGANO-AMIDES.

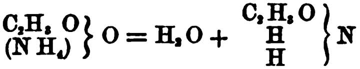
995. *Formation of the primary monamides.*—There are many ways of preparing this class of bodies. They can be produced,—1st. By the dry distillation of equal equivalents of chloride of ammonium and the dry soda salt of a monobasic organic acid, thus:—

Acetate of soda. Acetamide.



$$\left.\begin{array}{l}C_2H_3O\\\quad Na\end{array}\right\}O + NH_4Cl = NaCl + H_2O + \left.\begin{array}{l}C_2H_3O\\H\\H\end{array}\right\}N$$

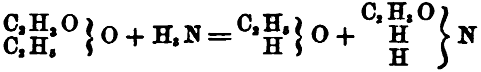
2nd. These primary amides differ from the corresponding ammoniacal salts by the elements of one atom of water. In some cases they can actually be prepared by simply distilling the corresponding ammonium salt, thus:—



$$\left.\begin{matrix}C_2H_3O\\(NH_4)\end{matrix}\right\}O = H_2O + \left.\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right\}N$$

3rd. By the action of ammonia upon the etherial salts of monobasic organic acids. At the common temperature, protracted contact is required; but under pressure, at temperatures between 110° and 120° C., the reaction is rapidly accomplished.

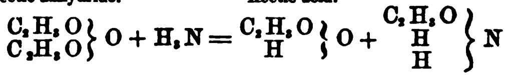
Acetic ether.



$$\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}O + H_3N = \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right\}N$$

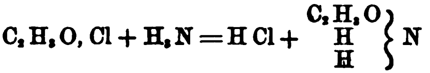
4th. By acting upon the organic anhydrides with ammonia, thus:—

Acetic anhydride. Acetic acid.



$$\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O + H_3N = \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right\}N$$

5th. By acting upon the chlorides of the acid radicals with gaseous ammonia, or with dry carbonate of ammonium. "This is the most general, rapid, and elegant process for the preparation of the monamides."



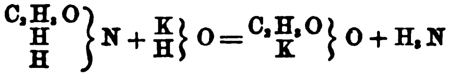
$$C_2H_3O,Cl + H_3N = HCl + \left.\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right\}N$$

EXERCISE.

177. Write out the formulæ of the following bodies:—Chloracetamide, butyramide, benzamide, trichloracetamide, nitrobenzamide, cinnamide, sulpho-phenylamide, propionamide, valeramide, cuminamide.

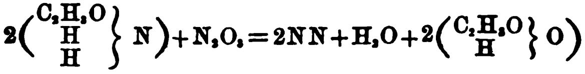
996. *Properties of the primary monamides.*—They are solid crystalline bodies, fusible and volatile at high temperature, without decomposition. By ebullition with alkalies they assimilate one atom of water, and produce

a corresponding monobasic organic acid, with disengagement of ammonia, thus:—



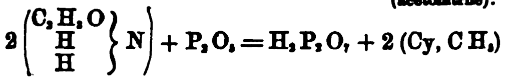
$$\left.\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right\}N+\left.\begin{matrix}K\\H\end{matrix}\right\}O=\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O+H_3N$$

2nd. Acted upon by nitrous acid, the corresponding organic acid is formed, and nitrogen disengaged,—



$$2\left(\left.\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right\}N\right)+N_2O_3=2NN+H_2O+2\left(\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O\right)$$

3rd. Acted upon by phosphoric anhydride, they abandon the elements of water, and become converted into the cyanides of the alcohol radicals (nitriles), thus:—



Cyanide of methyl (acetonitrile).

$$2\left(\left.\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right\}N\right)+P_2O_5=H_2P_2O_7+2\,(Cy,CH_3)$$

SECONDARY MONAMIDES.

997. Numerous members of this class have already been produced. It may, from the way the two equivalents of hydrogen in the ammonia are replaced, be divided into four groups.

1. Substitution of two monatomic acid radicals, either of the same or of different kind.
2. Substitution of one monatomic acid radical, and one monatomic alcohol radical. This class of bodies is named by Gerhardt *alcalamides*.
3. Substitution of one monatomic acid radical and one monatomic metal.
4. Substitution of one diatomic acid radical. These bodies were formerly termed *imides*,—a term which is still occasionally used.

998. *Preparation of the first group of secondary monamides.*—They can be obtained,—1st. By acting upon the primary monamides with hydrochloric acid; the primary body splitting up, under the influence of the acid, into the secondary monamide and ammonia, thus:—

$$\underset{\text{Acetamide.}}{2\left(\left.\begin{array}{c}C_2H_3O\\ H\\ H\end{array}\right\}N\right)} + HCl = H_4NCl + \underset{\text{Diacetamide.}}{\left.\begin{array}{c}C_2H_3O\\ C_2H_3O\\ H\end{array}\right\}N}$$

2nd. By treating the primary monamide with the chloride of a monatomic acid radical, thus:—

$$\left.\begin{array}{c}C_2H_3O\\ H\\ H\end{array}\right\}N + C_2H_3O, Cl = HCl + \left.\begin{array}{c}C_2H_3O\\ C_2H_3O\\ H\end{array}\right\}N$$

999. *Preparation of the second group of secondary monamides.*—The substances belonging to this group are formed by submitting the primary monamines to the several processes which, when applied to ammonia, furnish the primary monamides. The following are examples of this class:—

Methylacetamide -	$\left.\begin{array}{c}CH_3\\ C_2H_3O\\ H\end{array}\right\}N$	Phenylanisamide -	$\left.\begin{array}{c}C_6H_5\\ C_8H_7O_2\\ H\end{array}\right\}N$

1000. *Preparation of the third group of secondary monamides.*—These bodies are produced by the direct action of the amides upon the bases (oxides of mercury, silver, &c.), or upon their corresponding salts. They are decomposed by most of the acids which combine with the metal. When silver is the metal, the amide is violently attacked by the chlorides of the acid radicals, chloride of silver being formed, and a secondary monamide of the first group being produced. The following are examples of this class:—

Acetyl-zincamide (acetamidate of zinc) -	$\left.\begin{array}{c}C_2H_3O\\ Zn\\ H\end{array}\right\}N$	Bensoyl-mercuramide (benzamidate of mercury) - - -	$\left.\begin{array}{c}C_7H_5O\\ Hg\\ H\end{array}\right\}O$

1001. *Fourth group of secondary monamides.*—The following table includes nearly all the compounds of this kind which are at present known:—

Carbonylamide (cyanic acid) -	$\left.\begin{array}{c}CO''\\ H\end{array}\right\}N$
Sulpho-carbonylamide (sulpho-cyanic acid - - - -	$\left.\begin{array}{c}CS''\\ H\end{array}\right\}N$
Succinimide - - - -	$\left.\begin{array}{c}C_4H_4O_2''\\ H\end{array}\right\}N$

Citraconimide - - - -	$\left.\begin{matrix}C_5H_4O_2\\H\end{matrix}\right\}N$
Pyrotartrimide - - -	$\left.\begin{matrix}C_5H_6O_2{}'\\H\end{matrix}\right\}N$
Phtalimide - - - -	$\left.\begin{matrix}C_8H_4O_2{}'\\H\end{matrix}\right\}N$
Camphorimide - - -	$\left.\begin{matrix}C_{10}H_{14}O_2{}'\\H\end{matrix}\right\}N$

1002. "Some chemists are inclined to double the formulæ of this subdivision of the secondary monamides, and to view the imides as secondary diamides. For instance,—

Succinimide - - - - $\left.\begin{matrix}(C_4H_4O_2)_2{}''\\H_2\end{matrix}\right\}N_2$

There are, however, at present no experimental data on which this view can be safely founded.

1003. *Preparation of the imides.*—"The imides represent the acid ammonium salts of the dibasic acids, minus two equivalents of water, as the primary amides differ from ammoniacal salts of the monobasic acid by one equivalent of water.

$$\underset{\text{Acid succinate of ammonium.}}{\left.\begin{matrix}(C_4H_4O_2)'\\(H_4N)H\end{matrix}\right\}O_2} - 2H_2O = \underset{\text{Succinimide.}}{\left.\begin{matrix}(C_4H_4O_2)'\\H\end{matrix}\right\}N}$$

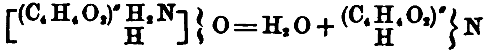
"This equation represents, in fact, the most general process of the formation of the imides. All the compounds mentioned in the above list, with the exception of carbonylamide, may be obtained by the distillation of the acid ammonium salts.

2nd. "They are also obtained by the action of ammonia on the anhydrides of the dibasic acids, thus:—

$$\underset{\text{Succinic anhydride.}}{\left.\begin{pmatrix}C_4H_4O_2\\C_4H_4O_2\end{pmatrix}''O_2\right\}} + 3H_3N = \underset{\text{Succinate of ammonium.}}{\left.\begin{matrix}(C_4H_4O_2)''\\(H_4N)_2\end{matrix}\right\}O_2} + \underset{\text{Succinimide.}}{\left.\begin{matrix}(C_4H_4O_2)''\\H\end{matrix}\right\}N}$$

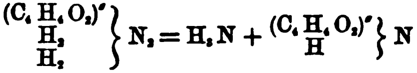
3rd. "The action of heat upon the primary monamidic acids, and on the primary diamides, likewise gives rise to secondary monamides. In illustration of this, the formation of succinimide in these reactions may be quoted:—

Succinamic acid. Succinimide.



$$\left[\begin{array}{c}(C_4H_4O_2)''\,H_2N\\ \quad\quad\quad\quad H\end{array}\right]\Big\}\,O = H_2O + \left.\begin{array}{c}(C_4H_4O_2)''\\ H\end{array}\right\}N$$

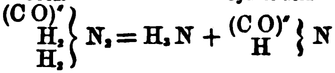
Succinyl-diamide (succinamide).



$$\left.\begin{array}{c}(C_4H_4O_2)''\\ H_2\\ H_2\end{array}\right\}N_2 = H_3N + \left.\begin{array}{c}(C_4H_4O_2)''\\ H\end{array}\right\}N$$

4th. "Cyanic acid (carbonylamide) has been lately obtained by a perfectly similar process, viz., the decomposition of a diamine under the influence of agents capable of fixing ammonia. Urea, distilled with anhydrous phosphoric acid, yields cyanic acid.

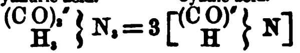
Urea. Cyanic acid.



$$\left.\begin{array}{c}(CO)''\\ H_2\\ H_2\end{array}\right\}N_2 = H_3N + \left.\begin{array}{c}(CO)''\\ H\end{array}\right\}N$$

5th. "Originally cyanic acid was produced by the action of heat on the triamide cyanuric acid.

Cyanuric acid. Cyanic acid.



$$\left.\begin{array}{c}(CO)_3'''\\ H_3\end{array}\right\}N_3 = 3\left[\left.\begin{array}{c}(CO)''\\ H\end{array}\right\}N\right]$$

1004. "The secondary monamides, like the primary ones, are solid crystalline bodies, fusible and volatile at high temperatures, without decomposition. Many of these bodies possess the character of weak acids, being, in fact, capable of exchanging the unreplaced equivalent of hydrogen for metals. Mixed with an ammoniacal solution of nitrate of silver, many of them yield well-defined silver salts.

1005. "Under the influence of acids and alkalies, the secondary monamides are converted into ammonia, and the acids from which they have been actually derived, or may be imagined derivable."

EXERCISES.

178. Write out the formulæ of the following bodies:—Diacetamide, benzoil-salicylamide, disulphophenyl-amide, sulphophenyl-benzamide, methyl-acetamide, ethyl-acetamide, phenyl-acetamide, phenyl-butyramide.

179. Describe as many different processes as possible for the preparation of the second group of secondary monamides.

TERTIARY MONAMIDES.

1006. This class may, from the way the three equivalents of hydrogen in the ammonia are replaced, be divided into seven groups:—

1. Substitution of three monatomic acid radicals for the three equivalents of H. No compound has hitherto been produced in which the three equivalents of H are replaced by three equivalents of the same monatomic acid radical.
2. Substitution of two monatomic acid radicals and one monatomic alcohol radical.
3. Substitution of two monatomic acid radicals and one monatomic metal.
4. Substitution of one monatomic and one diatomic acid radical.
5. Substitution of one diatomic acid radical and one monatomic alcohol radical.
6. Substitution of one diatomic acid radical and one monatomic metal.
7. Substitution of one triatomic radical. In this group the class of bodies called *nitriles* may be supposed to be placed.

1007. *First group of tertiary monamides.*—May be prepared in a variety of ways; the most general is by treating the first group of the secondary ones with the chloride of an acid radical. The alkalies decompose these compounds with evolution of ammonia, and reproduction of the acids of the radicals.

1008. *Second group of tertiary monamides.*—The most general way for preparing these bodies is by treating the second group of the secondary monamides with the chlorides of the acid radicals. The alkalies decompose them into monamines, and the acids whose radicals are present.

1009. *Third group of tertiary monamides.*—These bodies may be prepared in the same way as the members of the third group of secondary monamides, substituting, of course, a secondary monamide for the primary one.

1010. *Fourth group of tertiary monamides.*—By acting upon the imides with the chloride of an acid radical.

1011. *Fifth group of tertiary monamides.*—From the processes which have been already given for the preparation of monamines and monamides, a variety of ways for the preparation of these bodies will at once suggest themselves to the student. We will therefore only give the following very general one, reserving the others as an exercise for the students, by acting upon primary monamines with the chlorides of the diatomic acids.

1012. *Seventh group of tertiary monamides.*—The following mineral combinations belong to this class by their mode of formation or their reactions:—

Phosphamide - - - - -	$PO'' \}N$
Boramide - - - - - - -	$B'' \}N$
Free nitrogen, or nitrogen of nitrogen, or the amide of nitrous acid	$N'' \}N$
Protoxide of nitrogen, or the amide of nitric acid - - - -	$NO' \}N$

1013. When the ammonium salts of the monobasic organic acids are distilled with phosphoric auhydride, the salts are decomposed into two equivalents of water, which combine with the phosphoric compound, and into the class of bodies termed nitriles. Acetate of ammonia, for example, when it loses two equivalents of water, becomes transformed into acetonitrile.

$$\left.\begin{matrix}(C_2H_3O)\\(NH_4)\end{matrix}\right\} O - 2H_2O = C_2H_3,N.$$

1014. These nitriles, from their behaviour under the influence of reagents, resemble, in many respects, the origin and behaviour of the monamides in general, but they have, in addition, many peculiarities of their own. They may be formulated as tertiary monamides, in which the three atoms of hydrogen are replaced by a triatomic radical. The following is a list of these bodies, formulated as tertiary monamides:—

Formonitrile formylamide (prussic acid) - - - - -	$(CH)'' \}N$
Acetonitrile, vinylamide - -	$(C_2H_3)'' \}N$
Propionitrile, allylamide - -	$(C_3H_5)'' \}N$
Benzonitrile - - - - -	$(C_7H_5)'' \}N$
Cumonitrile - - - - -	$(C_{10}H_{11})'' \}N$

1015. These triatomic radicals have not been isolated, but we have a series of chlorides and bromides of these triatomic radicals. Examples:—

Bromoform	$(CH)''' Br_3$
Tribromide of vinyl	$(C_2H_3)''' Br_3$
Tribromide of allyl	$(C_3H_5)''' Br_3$

And we have also oxygen compounds of triatomic radicals, as—

Glycerin - - - - - $\left.\begin{matrix}(C_3H_5)''' \\ H_3\end{matrix}\right\} O_3$

These bromides can be converted into the nitriles by the action of ammonia.

1016. The formation of hydrocyanic acid by the action of acids on the metallic cyanides, and the facility with which the hydrogen in this acid is replaced by metals, altogether precludes, as Dr. Hofmann well observes, the idea of associating it with the carbon, in accordance with our present conception of the manner in which these two elements are united in organic molecules.

1017. The other nitriles, as well as formonitrile (prussic acid), may be obtained from cyanogen compounds by distilling a mixture of a sulphovinate of potassa with cyanide of potassium. Example:—

$$KCN + \left.\begin{matrix}(SO_2)'' \\ K(CH_3)\end{matrix}\right\} O_2 = \left.\begin{matrix}(SO_2)'' \\ KK\end{matrix}\right\} O_2 + C_2H_3N$$

These substances must therefore have at least two formulæ. Obtained by the action of phosphoric anhydride from the ammonium salts of the monobasic organic acids, they may be regarded, in this and other respects, as tertiary monamides. Produced by the action of the sulphovinates, they may be regarded as the cyanides of the alcohol radicals; thus, cyanide of methyl, acetonitrile, and vinylamide, are names given to the same substance. According to one mode of its formation, it may be formulated thus, CN, CH_3 (cyanide of methyl). According to another mode of its formation, it may be formulated thus, $(C_2H_3)''' \} N$ (vinylamide). These nitriles only yield up cyanogen under the influence of the most powerful agents of decomposition, such as potassium at high temperatures. Submitted to the action of alkalies and acids, they reproduce ammonia and salts of the acids from which they are derived.

1018. The student must now write out answers to the following questions:—

EXERCISES.

180. Write out the formulæ of the following bodies:—First group of tertiary monamides:—Sulphophenyl-dibenzamide, acetyl-sulphophenyl-benzamide, sulphophenyl-benzoyl-cuminamide. Second group:—Ethyl-diacetamide, phenyl-dibenzamide. Third group:—Diethyl-zincamide, sulphophenyl-benzoyl-argentamide, benzoyl-salicyl-argentamide. Fifth group:—Cyanate of ethyl (ethyl-carbonylamide), cyanate of phenyl, sulphocyanide of phenyl, phenyl-succinimide, phenyl-camphorimide. Sixth group:—Carbonyl-potassamide (cyanate of potassium), sulphocarbonyl-plumbamide (sulphocyanide of lead), succinyl-argentamide (succinimidate of silver).

181. What acids would be formed on treating acetonitrile, propionitrile, benzonitrile, cumonitrile, with acids or alkalies? and what would be the names of these different nitriles, if they are considered as the cyanides of the alcohol radicals? and how would you prepare them?

182. Give as many different processes as you can for the preparation of the fifth group of tertiary monamides.*

POLYAMMONIAS.

1019. By substituting polyatomic radicals for the hydrogen in ammonia, several ammonia molecules coalesce, the number depending upon the atomicity of the radical. These complex ammonias are often termed polyammonias, and they are subdivided into polyamines and polyamides, according to the chemical character they exhibit.

1020. The formation of polyammonias may be accomplished in at least three essentially different ways. For the present we shall only point out two of them. 1st. The ammonia molecules may be tied together by a polyatomic radical; the number of ammonia atoms which coalesce depending on the atomicity of the polyatomic radical. A diatomic radical, for example, would cause two atoms; a triatomic radical would cause three atoms; a tetratomic radical would cause four atoms of ammonia to unite together. This method may be expressed by the following general equation:—

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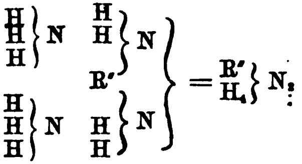
* The student must now study—first, the chlorides, &c., of the mon-onium bodies (page 385); 2nd, the hydrated oxides of the onium bodies (page 386); 3rd, the acid derivatives of ammonium (page 332). After he has gone through these groups, he commences the polyammonias.

$$R^{n} Br_{n} + n\, H_{3} N = (R^{n} H_{3n} N_{n})^{n} Br_{n}.$$

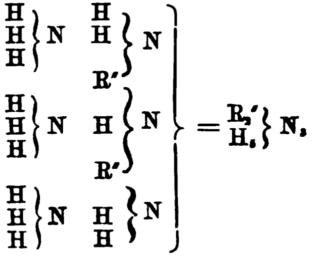
1021. According to the second plan, the accumulation of the ammonia molecules may be attempted by increasing the number of polyatomic radicals of given atomicity used as binding materials. It is obvious that, theoretically, any number of ammonia molecules may be held together by diatomic radicals, provided we appropriately increase the number of the latter, thus:—

Diamine.



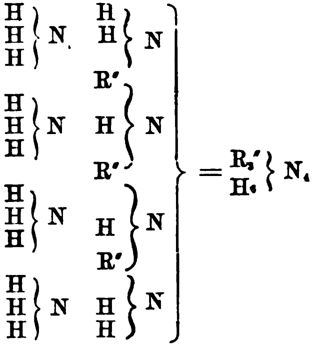
$$\left.\begin{matrix} \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N & \left.\begin{matrix}H\\H\end{matrix}\right\}N \\ & R' \\ \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N & \left.\begin{matrix}H\\H\end{matrix}\right\}N \end{matrix}\right\} = \left.\begin{matrix}R'\\H_{4}\end{matrix}\right\}N_{2}$$

Triamine.



$$\left.\begin{matrix} \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N & \left.\begin{matrix}H\\H\end{matrix}\right\}N \\ & R' \\ \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N & \left.\begin{matrix}H\end{matrix}\right\}N \\ & R' \\ \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N & \left.\begin{matrix}H\\H\end{matrix}\right\}N \end{matrix}\right\} = \left.\begin{matrix}R_{2}'\\H_{6}\end{matrix}\right\}N_{3}$$

Tetramine.



$$\left.\begin{array}{l} \left.\begin{array}{l}H\\H\\H\end{array}\right\}N \quad \left.\begin{array}{l}H\\H\end{array}\right\}N \\ \qquad\qquad\; R' \\ \left.\begin{array}{l}H\\H\\H\end{array}\right\}N \quad \left.\begin{array}{l}H\end{array}\right\}N \\ \qquad\qquad\; R' \\ \left.\begin{array}{l}H\\H\\H\end{array}\right\}N \quad \left.\begin{array}{l}H\\R'\end{array}\right\}N \\ \left.\begin{array}{l}H\\H\\H\end{array}\right\}N \quad \left.\begin{array}{l}H\\H\end{array}\right\}N \end{array}\right\} = \left.\begin{array}{l}R_3'\\H_6\end{array}\right\}N_4$$

1022. The accumulation of ammonia molecules is determined, as shown by these general examples, by the number of diatomic radicals which are fixed; that for the production of an $(n + 1)$ atomic ammonia, at least n diatomic radicals are required; the number of molecules of diatomic bromides and the quantity of ammonia involved in the accumulative processes, are given in the following general equation:—

$$nR'Br_2 + 2nH_3N = \left[R_n'H_{(2n+4)}N_{(n+1)}\right]^{(n+1)}Br_{(n+1)} + n - 1\left([H_4N]\,Br\right)$$

1023. We will now show how this equation applies to the first terms of the series of diammonium, triammonium, and tetrammonium salts.

1. When $n = 1$ the equation gives us the first term of a series of diammonium compounds, for—

$$R'Br_2 + 2H_3N = \left[R'H_6N_2\right]'Br_2;$$

and if $R' =$ the diatomic body ethylene $(C_2H_4)'$, we obtain, in this manner, the dibromide of ethylene-diammonium,—

$$C_2H_4Br_2 + 2H_3N = \left[(C_2H_4)'H_6N\right]'Br_2.$$

2. When $n = 2$, the equation, it will be seen, gives us the first term of a series of triammonium compounds.

$$2\,R'Br_2 + 4\,H_3N = \left[R'_2 H_8 N_3\right]'' Br_3 + \left[H_4N\right]Br;$$

and if $R' = (C_2H_4)'$, we obtain the tribromide of diethylene-triammonium.

$$2\left([C_2H_4]'Br_2\right) + 4\,H_3N = \left[(C_2H_4)_2' H_8N_3\right]'' Br_3 + \left[(H_4N)\,Br\right]$$

3. When $n = 3$, the equation gives us the first term in the series of tetrammonium compounds, thus:—

$$3\,R''Br_2 + 6\,H_3N = \left[R_3' H_{10} N_4\right]'''' Br_4 + 2\left([H_4N]\,Br\right);$$

and if $R' = (C_2H_4)'$ we obtain the tetrabromide of triethylene-tetrammonium.

$$3\left([C_2H_4]'Br_2\right) + 6\,H_3N = \left[(C_2H_4)_3' H_{10}N_4\right]'' Br_4 + 2\left([H_4N]\,Br\right)$$

1024. Just as we have seen that the hydrogen in ammonia can be gradually replaced by equal equivalents of the radicals of the vinic alcohol series, so the atoms of the hydrogen in the polyammonias can be gradually replaced by polyatomic radicals; as examples of this, we will contrast the series of monamines, diamines, and triamines.

Ethylamine. $\left.\begin{matrix}(C_2H_5)'\\ H\\ H\end{matrix}\right\}N$	**Ethylene-diamine.** $\left.\begin{matrix}(C_2H_4)''\\ H_2\\ H_2\end{matrix}\right\}N_2$	**Diethylene-triamine.** $\left.\begin{matrix}(C_2H_4)''\\ (C_2H_4)''\\ H_5\end{matrix}\right\}N_3$
Diethylamine. $\left.\begin{matrix}(C_2H_5)'\\ (C_2H_5)\\ H\end{matrix}\right\}N$	**Diethylene-diamine.** $\left.\begin{matrix}(C_2H_4)''\\ (C_2H_4)''\\ H_2\end{matrix}\right\}N_2$	**Triethylene-triamine.** $\left.\begin{matrix}(C_2H_4)''\\ (C_2H_4)''\\ (C_2H_4)''\\ H_3\end{matrix}\right\}N_3$
Triethylamine. $\left.\begin{matrix}(C_2H_5)'\\ (C_2H_5)'\\ (C_2H_5)'\end{matrix}\right\}N$	**Triethylene-diamine.** $\left.\begin{matrix}(C_2H_4)''\\ (C_2H_4)''\\ (C_2H_4)''\end{matrix}\right\}N_2$	**Tetrethylene-triamine.** $\left.\begin{matrix}(C_2H_4)''\\ (C_2H_4)''\\ (C_2H_4)''\\ (C_2H_4)''\\ H\end{matrix}\right\}N_3$

1025. We have seen that four different compounds can be formed if each equivalent of hydrogen in ammonium be successively replaced by a monatomic radical. So, also, four compounds can be formed if each double equivalent of hydrogen in *diammonium* be successively replaced by a diatomic radical. But the group of triatomic ethylene-ammoniums does not comprise less than five compounds, the last term of the series being a non-volatile body, the hydrate of the triatomic ethylene-ammonium, in which the twelve equivalents of hydrogen in three equivalents of ammonium have been replaced by six equivalents of ethylene; this body is, therefore, represented on the water type, and by the following formula:—

$$\left.\begin{array}{c}\left[(C_2H_4)_6'' N_3\right]''' \\ H_3\end{array}\right\} O_3$$

1026. But not only is there produced by the action of bibromide of ethylene on ammonia a series of four diammoniums, but there are also formed four different series of monammoniums, each series consisting of four ammoniums; so that, even when omitting secondary products, sixteen compounds are capable of being produced by the action of bibromide of ethylene on ammonia.

1027. The four ammonium compounds in the series of diammoniums would have the following formulæ:—

$$\begin{array}{l|l}(C_2H_4)'' H_6 N_2 Br_2 & (C_2H_4)_3'' H_2 N_2 Br_2 \\ (C_2H_4)_2'' H_4 N_2 Br_2 & (C_2H_4)_4'' \quad N_2 Br_2\end{array}$$

1028. Along with this series of diammoniums, a series of monammoniums is always formed, in which monobromide of ethylene (C_2H_4Br) enters as a monatomic radical; the four monammoniums which could thus be formed would have the following composition:—

$$\begin{array}{l|l}(C_2H_4Br)' H_3 N Br & (C_2H_4Br)_3' H N Br \\ (C_2H_4Br)_2' H_2 N Br & (C_2H_4Br)_4' \quad N Br\end{array}$$

1029. If the reaction by which the last series of monammoniums is formed takes place in the presence of water, the bromine, which is either wholly or partially eliminated as hydrobromic acid, is replaced by the molecular residue of water; and thus a series of monammonium salts is formed, in which a molecule ($C_2H_4HO = C_2H_5O$) enters monatomically. The salts in this series would have the following formulæ:—

$$\begin{array}{l|l} (C_2H_5O)'\ H_3N\,Br & (C_2H_5O)_3\,H\,N\,Br \\ (C_2H_5O)_2'\ H_2N\,Br & (C_2H_5O)_4\quad N\,Br \end{array}$$

1030. As ethylene compounds have a tendency to resolve themselves, in the presence of alkalies, into vinyl compounds, a fourth series of monammoniums, in which vinyl (C_2H_3) enters as a monatomic radical, is formed. Four ammoniums in this series would have the following formulæ:—

$$\begin{array}{l|l} (C_2H_3)'\ H_3N\,Br & (C_2H_3)_3'\ H\ N\,Br \\ (C_2H_3)_2'\ H_2N\,Br & (C_2H_3)_4'\quad N\,Br \end{array}$$

1031. Ammonia, we have already stated, is capable of producing (omitting secondary products), by the action of bibromide-ethylene, not less than sixteen compounds; ethylamine, by the action of the same reagent, not more than twelve; diethylamine not more than eight; and triethylamine not more than four compounds. The reason why fewer compounds are formed with an amine, in which one equivalent of hydrogen is replaced by a monatomic radical, than with ammonia itself, and why the number decreases by four for each atom of hydrogen that is replaced in the ammonia by a monatomic radical, will suggest itself, no doubt, to the diligent student.

1032. The student will naturally ask, How did Hofmann prove that the two equivalents of bromine, which exist in every one equivalent of the ammonium compounds in which he states (C_2H_4Br) enters monatomically, exist in two different states? He proved it in the following manner:—

1. If nitrate of silver is added to one of these monammonium salts—say, bromide of bromethylene triethylammonium,—you only get one-half the bromine precipitated as bromide of silver: even if the solution containing the nitrate of silver and the ammonium compound be boiled for a lengthened period, the other half of the bromine remains untouched; the change which the nitrate of silver undergoes is, therefore, very simple, thus:—

$$\left[(C_2H_4Br)'(C_2H_5)_3NBr\right] + \left.\begin{matrix}Ag\\NO_2\end{matrix}\right\}O =$$

$$\left[(C_2H_4Br)'(C_2H_5)_3\left.\begin{matrix}N\\NO_2\end{matrix}\right\}O\right] + AgBr$$

2. If freshly precipitated oxide of silver is added, instead of nitrate of silver, to the ammonium compound, the whole of the bromine is separated at once in the form of bromide of silver, a new base being formed. According to circumstances, this base may contain, in place of the brominated radical, the radical vinyl (C_2H_3), or another radical, arising from the brominated radical, by the substitution of the residue HO for Br; the formula of this radical is, therefore, $C_2H_4HO = C_2H_5O$.

(*a.*) When the base containing the vinyl radical is formed, the following changes take place:—

$$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\\(C_2H_4Br)'\end{matrix}\right\}NBr + \left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O = \left[(C_2H_5)_3(C_2H_3)'\left.\begin{matrix}N\\H\end{matrix}\right\}O\right] + 2AgBr$$

(*b.*) Acetate of silver acts differently to the nitrate upon those monammonium compounds containing the brominated radical; the acetate does not act upon the bromide of the bromethylene triethylammonium in the anhydrous condition, but in the presence of alcohol or water, at a temperature of 100° C., it speedily removes the whole of the bromine, acetate of vinyl-triethylammonium being formed, thus:—

$$\left[(C_2H_4Br)(C_2H_5)_3NBr\right] + 2\left(\left.\begin{matrix}C_2H_3O\\Ag\end{matrix}\right\}O\right) =$$

Acetate of vinyl-triethylammonium.

$$2AgBr + \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O + \left[\left.\begin{matrix}(C_2H_3O)\\(C_2H_3)(C_2H_5)_3N\end{matrix}\right\}O\right]$$

(*c.*) The base containing the radical (C_2H_5O) is always formed when the action takes place in moderately dilute solutions; the following changes take place when his base is formed:—

$$\left[(C_2H_4Br)'(C_2H_5)_3N\right]Br + \left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}O =$$

$$2AgBr + \left[(C_2H_5O)(C_2H_5)_3\left.\begin{matrix}N\\H\end{matrix}\right\}O\right]$$

1033. The *oxethylated* base can be converted into the bromethylated one, by adding to the chloride of the former pentabromide of phosphorus; the ammonium compound is energetically attacked by the bromide of phosphorus, oxybromide of phosphorus and hydrobromic acid are abundantly evolved, and the residue of the reaction contains the chloride of bromethylene triethylammonium, thus:—

$$\left[(C_2H_5O)(C_2H_5)_3N\right]Cl + PBr_5 = HBr + POBr_3 + \left[(C_2H_4Br)(C_2H_5)_3N\right]Cl$$

Thus the monatomic radical (C_2H_5O) in this ammonium compound, which we have seen originally sprung out of the bibromide of the diatomic radical ethylene, suffers, under the influence of pentabromide of phosphorus, alterations identical with those which it is known to undergo under similar circumstances, when conceived as a constituent of alcohol.

1034. Hofmann has pointed out that the salts of bromethylated and oxethylated triethylammonium may be regarded as tetrethylammonium salts, in which an equivalent of hydrogen in one of the ethyl atoms is replaced by bromine and by the residue HO respectively. Examples:

Bromide of tetrethylammonium	$\left[(C_2H_4H)\ (C_2H_5)_3N\right]Br$
Bromide of bromethylated triethylammonium - - -	$\left[(C_2H_4Br)\ (C_2H_5)_3N\right]Br$
Bromide of oxethylated triethylammonium - - -	$\left[(C_2H_4HO)\ (C_2H_5)_3N\right]Br$

1035. He has even proved that the bromethylated compound can be converted, simply by reduction, into a salt of tetrethylammonium. This transformation can be effected without difficulty, on acidulating the solution of the bromethylated bromide with sulphuric acid, and digesting the mixture with granulated zinc; the latent bromine is eliminated as hydrobromic acid, its place being at the same time filled by one equivalent of hydrogen, thus:—

$$\left[(C_2H_4Br)(C_2H_5)_3N\right]Br + HH = HBr + \left[(C_2H_5)_4N\right]Br$$

1036. We have stated that the polyammonias may be formed in at least three essentially different ways. We have already pointed out two of those methods; we shall now point out the third, which is the most singular plan of the three; for by this third method polyammonias are formed from the action of monatomic radicals.

3rd Method.—These bromethylated ammonias, when brought in contact with ammonia, or with a primary, secondary, or tertiary amine, coalesce with the added ammonia, a diammonium being the result. Thus, if we add together equal equivalents of bromide of bromethylated triethylammonium, and triethylamine, dibromide of ethylene hexethylated diammonium is produced, thus:—

$$\left[(C_2H_4Br)'(C_2H_5)_3N\right]'Br + \left[(C_2H_5)_3N\right] =$$
$$\left[(C_2H_4)''(C_2H_5)_6N_2\right]''Br_2$$

(*a.*) We noticed (906) that the hydrogen atoms in ethyl and its homologues can be replaced by bromine, chlorine, iodine, therefore we can obtain, by the substitution of one atom of bromine for one atom of hydrogen in bromide of ethyl, a body isomeric with bibromide of ethylene. Hofmann has made this body monobrominated bromide of ethyl $(C_2H_4Br)Br$; it has a different boiling point, and its other physical characters are altogether different to bibromide of ethylene, yet its behaviour is the same as bibromide of ethylene with ammonia or an amine,—the bromethylated ammonium is produced, which unites with ammonia or an amine in equivalent proportions, a diammonium being produced.

(*b.*) Polyammonias can, therefore, be formed by introducing into a body, on the type ammonia, a brominated monatomic radical: the bromide thus inserted is capable of fixing a body on the type ammonia, producing a polyammonia. The number of atoms of ammonia which are fixed will depend obviously upon the bromination of the monatomic radical: if one atom of hydrogen in the radical has been replaced by its equivalent of bromine, one atom of ammonia will be fixed; if two atoms of hydrogen in the radical have been replaced by equivalent quantities of bromine, two atoms of ammonia will be fixed, &c., thus:—

$$\left[(C_2H_3Br_2)'H_3N\right]Br + 2H_3N = \left[(C_2H_3)'''H_9N_3\right]'''Br_3$$
$$\left[(C_2H_2Br_3)'H_3N\right]Br + 3H_3N = \left[(C_2H_2)''''H_{12}N_4\right]''''Br_4$$

$$\left[(C_2 H Br_4)' H_3 N\right] Br + 4 H_3 N = \left[(C_2 H)'''' H_{15} N_5\right]'''' Br_5$$

$$\left[(C_2 \quad Br_5)' H_3 N\right] Br + 5 H_3 N = \left[(C_2 \quad)'''' H_{18} N_6\right]'''' Br_6$$

1037. But the ammonia can be fixed as well by increasing the number of atoms of the *mono*brominated monatomic radical as by increasing the number of atoms of bromine in one atom of the monatomic radical, thus :—

$$\left[(C_2 H_4 Br)_2 H_2 N\right] Br + 2 H_3 N = \left[(C_2 H_4)_2' H_8 N_3\right]'' Br_3$$

$$\left[(C_2 H_4 Br)_3 H \ N\right] Br + 3 H_3 N = \left[(C_2 H_4)_3' H_{10} N_4\right]''' Br$$

$$\left[(C_2 H_4 Br)_4 \quad N\right] Br + 4 H_3 N = \left[(C_2 H_4)_4' H_{12} N_5\right]'''' Br_5$$

1038. Marsh gas gives birth, by the gradual substitution of chlorine for its hydrogen, to four other bodies: thus we have,—

Marsh gas - - - -	$C_4 H_4$	- Tetrahydride of carbon.
Monochlorinated marsh gas -	$C H_3 Cl$	- Chloride of methyl.
Dichlorinated marsh gas -	$C H_2 Cl_2$	- Dichloride of methylene.
Trichlorinated marsh gas -	$C H Cl_3$	- Trichloride of formyl.
Tetrachlorinated marsh gas -	$C Cl_4$	- Tetrachloride of carbon.

1038. Dr. Hofmann was anxious to ascertain whether the four chlorinated derivatives, when submitted to the action of triethyl-phosphine, would fix respectively one, two, three, and four molecules of the phosphorus base, giving rise to the formation of mon, di, tri, and tetraphosphonium compounds. He had previously fixed one molecule of triethyl-phosphine with chloride of methyl, chloride of methyl-triethyl-phosphonium being formed. He had also proved that chloroform fixes three equivalents of the phosphorus base, the trichloride of formyl-nonethyl-triphosphonium being formed. It only remained for him to examine the action of the second and fourth chlorine compound. The dichloride of methylene is capable of fixing, he finds, either one or two molecules of phosphorus base; the formation of the ephemeral diatomic base being invariably preceded by that of the more stable chloromethylated monophosphonium compound. Although Dr. Hofmann has not yet succeeded in obtaining the direct product of the action of tetrachloride of carbon on triethyl-phosphine, yet the study of the products of decomposition have proved that the direct product is a mixture of two chlorides, viz.,—

Tetrachloride of carbo-dodeca-ethyl-tetraphosphonium,—

$$C_{25}H_{60}P_4Cl_4 = \left[C'''' \begin{array}{l} (C_2H_5)_3P \\ (C_2H_5)_3P \\ (C_2H_5)_3P \\ (C_2H_5)_3P \end{array} \right]'''' Cl_4$$

and trichloride of chlorocarbo-nonethyl-triphosphonium,—

$$C_{19}H_{45}P_3Cl_4 = \left[(C\,Cl)''' \begin{array}{l} (C_2H_5)_3P \\ (C_2H_5)_3P \\ (C_2H_5)_3P \end{array} \right]''' Cl_3$$

1039. "These experiments prove that the number of molecules of triethyl-phosphine, which, under favorable circumstances, can be fixed by the chlorinated derivatives of marsh gas, is determined by the number of chlorine equivalents which these substances contain."

1040. "The chlorinated derivatives of marsh gas exhibit, in their deportment with the phosphorus bases, the characters of hydrochloric acid. The monochlorinated product has the saturating capacity of one molecule of hydrochloric acid, the dichlorinated product of one or two molecules; the trichlorinated of one, two, or three molecules; the tetrachlorinated product, lastly, of one, two, three, or four molecules:—

$$\begin{array}{lllll} C\,H_3Cl & = (C\,H_3)'\;Cl & & & \\ C\,H_2Cl_2 & = (C\,H_2Cl)'\,Cl & = (C\,H_2)''\;Cl_2 & & \\ C\,H\,Cl_3 & = (C\,H\,Cl_2)'\,Cl & = (C\,H\,Cl)''\,Cl_2 & = (C\,H)'''\;Cl_3 & \\ C\,Cl_4 & = (C\,Cl_3)'\;Cl & = (C\,Cl_2)''\;Cl_2 & = (C\,Cl)'''\;Cl_3 & = C''''\,Cl_4 \end{array}$$

1041. "The action of chloride of methyl on triethyl-phosphine produces only one salt; that of dichloride of methylene produces two; chloroform is capable of producing three; and tetrachloride of carbon four salts."

Monochlorinated marsh gas.

Monatomic compound - $[(C\,H_3)(C_2H_5)_3P]\,Cl$

Dichlorinated marsh gas.

Monatomic salt - - - $[(C\,H_2Cl)'(C_2H_5)_3P]'\,Cl$

Diatomic salt - - - $[(C\,H_2)''(C_2H_5)_6P_2]''\,Cl_2$

Trichlorinated marsh gas.

Monatomic salt	$[(C\,H\,Cl_2)'\,(C_2\,H_5)_3\,P]\,Cl$
Diatomic salt	$[(C\,H\,Cl)''\,(C_2\,H_5)_6\,P_2]''\,Cl_2$
Triatomic salt	$[(C\,H)'''\,(C_2\,H_5)_9\,P_3]'''\,Cl_3$

Tetrachlorinated marsh gas.

Monatomic salt	$[(C\,Cl_3)'\,(C_2\,H_5)_3\,P]\,Cl$
Diatomic salt	$[(C\,Cl_2)''\,(C_2\,H_5)_6\,P_2]''\,Cl_2$
Triatomic salt	$[(C\,Cl)'''\,(C_2\,H_5)_9\,P_3]'''\,Cl_3$
Tetratomic salt	$[C''''\,(C_2\,H_5)_{12}\,P_4]''''\,Cl_4$

1042. Many of the polyammonias can form as many different classes of salts as the numbers of molecules of ammonia they contain. Thus the triammonias are capable of forming three classes of salts, which may be generally represented as,—

$$R_2''\,H_5\,N_3.\,3\,H\,Cl$$
$$R_2''\,H_5\,N_3,\,2\,H\,Cl$$
$$R_2''\,H_5\,N_3,\,H\,Cl$$

1043. *Diagnosis of the polyammonias.*—But the student may ask, What proof is there that the ammonia atoms have coalesced under the influence of the polyatomic radicals? Why not divide the formulæ of the diammoniums by two; the triammoniums by three; and the tetrammoniums by four? We should then in each case obtain a formula which only contained one equivalent of nitrogen in what would be one equivalent of the body. We will answer this question, not by supposed cases, but by what has really occurred.

1044. Some years before Dr. Hofmann attempted the formation of polyammonias, M. Cloëz obtained three bases on submitting ammonia to the action of bibromide of ethylene. To these three bases he assigned the following formulæ and names:—

Formylia	$C\,H_3\,N$
Acetylia	$C_2\,H_5\,N$
Propylia	$C_3\,H_7\,N$

1045. When Dr. Hofmann began to search for the diammonium bodies, he studied the results obtained by M. Cloëz, and he was led to doubt the correctness of the formulæ assigned to these three bodies by that chemist, for the following reasons :—

1st. It is difficult to understand how the action of ammonia upon a compound like the Dutch liquid can produce simultaneously three bodies belonging to three different homologous families, the formyl-, acetyl-, and propyl-series.

2nd. These doubts are increased if we examine into the physical characters of these bodies, especially if we consider their high boiling-points, and the differences which the three bases exhibit in this respect :—

		Boiling point.	
Formylia -	- CH_3N -	123°	difference 47
Acetylia -	- C_2H_5N -	170	difference 40
Propylia -	- C_3H_7N -	210	

Methylamine (CH_5N), which contains only two equivalents of hydrogen more than formylia, is a gas at the common temperature, and its point of liquefaction is considerably below the freezing point of water. Again, the differences of the boiling points of substances, related in the way that the formulæ of M. Cloëz suppose, do not often exceed 20°, and very rarely rise to 40° and 47°. All these difficulties disappear if the formulæ are doubled; they then become diammonium bases, in which two, four, or six equivalents of hydrogen are replaced respectively by one, two, or three equivalents of the biatomic radical ethylene. Formylia thus becomes monethylene-diamine; acetylia becomes diethylene-diamine; and propylia becomes triethylene-diamine. The analyses agree better with the double than with the single formulæ; for instance, the analysis of the hydrochlorate of the base formylia furnished Hofmann with the following results :—

	Required for the formula of M. Cloëz.	Required for Dr. Hofmann's formula.	Mean of Analysis.
Carbon -	- 18·32 -	- 18·04 -	- 17·87
Hydrogen	- 6·10 -	- 7·51 -	- 7·55
Chlorine	- 54·19 -	- 53·38 -	- 53·17

The student will remark that the hydrogen is greatly in excess of that required by Mr. Cloëz's formula. Even in that chemist's analysis the quantity obtained exceeded what was required by his formula by 1·28 per cent.; and in the analysis of the hydrated base, and the anhydrous base, he obtained 12·77 and 13·31 of hydrogen; whereas for his formula he required only 10·52 and 10·34; whilst 12·82 and 13·38 were required for Hofmann's formula.

1046. To these objections and arguments brought forward by Hofmann, M. Cloëz gave the following reply:—"According to the hypothesis of Hofmann, the action of ammonia on the chlorinated and brominated hydrocarbons cannot give rise to the formation of chloride or bromide of ammonium. The reaction consists simply in a combination of the two substances without the separation of a third compound. It is a case of symmorphosis, or addition, thus:—

$$(C_2H_4)Cl_2 + 2\,H_3N = (C_2H_4)\,H_4N_2,\,2\,H\,Cl.$$

Experiment proves, however, that the reaction involves the elimination of hydrochloric acid, and the fixation of the elements of amidogen. Apomorphosis and symmorphosis are accomplished side by side, as indicated by the following equation:"—

$$C_2H_4Cl_2 + 2\,H_3N = (C_2H_3)\,H_2N,\,H\,Cl + H_3N,\,H\,Cl.$$

1047. "But there is, said M. Cloëz, "a capital fact, which completely settles the question at issue,—this is the vapour density of the free base. This density has been found by experiment to be 1·42. The theoretical density calculated for my formula, referred to two volumes, is 1·315; the modified formula of M. Hofmann, likewise referred to two volumes, gives the theoretical density of 2·699. These results appear to me decisive; and I do not hesitate to maintain the formulæ of the new series of bases of which I first pointed out the formation."

1048. Dr. Hofmann replied that M. Cloëz would be perfectly right in assuming that his (Dr. Hofmann's) hypothesis involved the non-formation of chloride or bromide of ammonium, if, during the reaction, no other base were formed, except the first one (monethylated diammonium); "but he forgets altogether that in the process under examination, exactly as in the mutual reaction between bromide of ethyl and ammonia, several other bases of more advanced substitution are produced. The equations which I give for the formation of these bodies likewise involve the elimination of bromide of ammonium, and, in fact, of considerable quantities of this compound, thus:—

$$2\,(C_2H_4)''\,Br_2 + 4\,H_3N = (C_2H_4)_2''\,H_2N_2,\,2\,H\,Br + \\ 2\,(H_3N,\,H\,Br)$$

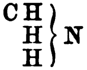
$$3\,(C_2H_4)''\,Br_2 + 6\,H_3N = (C_2H_4)_3''\,N_2,\,2\,H\,Br + \\ 4\,(H_3N,\,H\,Br)$$

1049. "The bromide of ammonium, which thus separates in considerable quantity in the action of dibromide of ethylene upon ammonia, belongs to the second and third portion of the reaction; it has nothing whatever to do with the formation of the first base. M. Cloëz, as I have pointed out, does not admit the simple equation which I have given for the formation of this body; he denies that it is simply formed by the union of the two compounds reacting upon each other. According to his opinion, it is produced in a secondary reaction, occasioned by the intervention of heat. My experiments do not confirm this opinion. A mixture of dibromide of ethylene and alcoholic ammonia, allowed to stand for some time at the ordinary temperature, deposited a quantity of crystals, from which I was enabled to extract, without distillation, simply by successive crystallizations, absolutely pure salt of ethylene-diamine, as proved by the analysis of the bromide, the chloride, and the platinum salt."

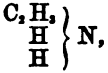
1050. Hofmann said that he perfectly agreed with M. Cloëz as to the importance of the vapour densities; but he showed that the hydrated base which that chemist employed is split up, as we have already noticed (336), into water and the anhydrous base; each of these compounds, the water and the anhydrous base, occupying two volumes. Hofmann, therefore, determined the vapour density of the anhydrous base; this gave the number, 2·00, which absolutely coincides with the theoretical density of the diatomic formula ($C_2H_8N_2$) referred to two volumes. This theoretical density is 2·07; whilst the formula of M. Cloëz, likewise referred to two volumes, requires the theoretical density of 1·00. Hofmann thus remarks:—"The molecule of *ethylene-diamine*, then, like those of all other well-examined organic compounds, corresponds to two volumes of vapour; and the vapour density of the base, far from militating against the molecular value which I assign to this body, furnishes, on the contrary, an additional and incontestable argument in its favour."

1051. Hofmann goes on to remark, "The preceding experiments, although fixing in a satisfactory manner the composition and the equivalents of the two diammonias, do not unveil their molecular constitution—their degree of substitution." He endeavoured to solve this problem in the same way as he had done the monammonias (983), by submitting them to the action of iodide of ethyl; this process, *moreover, could not fail to furnish a final decision between the two theories.*

1052. "In considering, with M. Cloëz, the two bases as primary monamines belonging respectively to the formic and to the acetic groups,—

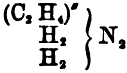


$$\left.\begin{matrix}CH\\H\\H\end{matrix}\right\}N$$

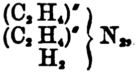


$$\left.\begin{matrix}C_2H_3\\H\\H\end{matrix}\right\}N,$$

it is evident that each of them must be capable of absorbing successively one, two, or three equivalents of ethyl, and yielding three ethylated bases, two volatile and one fixed. On the contrary, if the bases were products of the successive substitution of the same molecule for the hydrogen in two equivalents of ammonia, if they were respectively a primary and a secondary diamine,—



$$\left.\begin{matrix}(C_2H_4)''\\H_2\\H_2\end{matrix}\right\}N_2$$



$$\left.\begin{matrix}(C_2H_4)''\\(C_2H_4)''\\H_2\end{matrix}\right\}N_2,$$

the first of the two must likewise give rise to the formation of three bases, whilst the second one would produce only two." Experiment verified this anticipation of Hofmann's. In submitting the base, which he regarded as ethylene-diamine, to the alternate action of iodide of ethyl and oxide of silver, he succeeded in obtaining two volatile ethylated bases, and a third one, which is fixed. These compounds are well defined; their composition was established by the analysis of their iodides, or their platinum salts. Represented as salts, these bases contain,—

Salt of ethylene-diammonium - - -	$\left[(C_2H_4)'' \quad H_6N_2\right]I_2$
Salt of diethylated ethylene-diammonium - -	$\left[(C_2H_4)''(C_2H_5)_2 \quad H_4N_2\right]I_2$
Salt of tetrethylated ethylene-diammonium - -	$\left[(C_2H_4)''(C_2H_5)_4 \quad H_2N_2\right]I_2$
(Salt of pentethylated ethylene-diammonium -	$\left[(C_2H_4)''(C_2H_5)_5 \quad HN_2\right]I_2)$
Salt of hexethylated ethylene-diammonium - -	$\left[(C_2H_4)''(C_2H_5)_6 \quad N_2\right]I_2$

1053. On repeating the same experiments with the base, which he regarded as ethylene-diamine, he observed perfectly analogous phenomena; but the reaction yielded only one volatile base, which was immediately converted into a fixed base. Analysed in a similar manner, and represented as salts, these bases exhibit the following composition:—

Salt of diethylene-diammonium - - -	$\left[(C_2H_4)_2'' \quad H_4N_2\right]I_2$
Salt of diethylated diethylene-diammonium - -	$\left[(C_2H_4)_2''(C_2H_5)_2 \quad H_2N_2\right]I_2$
(Salt of triethylated diethylene-diammonium	$\left[(C_2H_4)_2''(C_2H_5)_3 \quad HN_2\right]I_2)$
Salt of tetrethylated diethylene-diammonium	$\left[(C_2H_4)_2''(C_2H_5)_4 \quad N_2\right]I_2$

1054. In the case of diamines, the substitution of ethyl, or any monatomic radical, has never been limited to the substitution of single atoms; two or four atoms of ethyl always go in and replace the like number of atoms of hydrogen; but in the case of diammoniums it is different; the two hydrogen atoms of the diammoniums can be replaced singly; we can have, therefore, $(R''R_4'HN_2)I_2$, or $(R''R_5N_2)I_2$. Now as a monamine thus treated with iodide of ethyl or methyl, can yield only *one* compound (R_4I), this character of the diammoniums, in retaining one equivalent of unreplaced hydrogen, will facilitate the diagnosis of the diamines, especially in the case of compounds easily decomposable, or difficultly accessible; and it may, under certain conditions, become the principal criterion for ascertaining the atomicity of an ammonia.

1055. The pentethylated compound $\left[R''_2(C_2H_5)_5HN_2\right]''I_2$ is always formed when the secondary diamine is submitted to the action of iodide of ethyl. In this case two independent reactions are accomplished side by side. The first one transforms the diethylated diamine into a tetrethylated diammonium compound, thus:—

$$\left.\begin{matrix}(R_2)''\\(C_2H_5)_2\\H_2\end{matrix}\right\}N_2+2\left[(C_2H_5)I\right]=\left[\left.\begin{matrix}(R)_2''\\(C_2H_5)_2\\(C_2H_5)_2\\H_2\end{matrix}\right\}N_2\right]''I_2$$

The second reaction gives rise to a pentethylated diammonium compound, while the iodide of the diethylated diammonium is reproduced, thus:—

$$3\left[\left.\begin{matrix}(R)_2''\\(C_2H_5)_2\\H_2\end{matrix}\right\}N_2\right]+6\left[(C_2H_5)I\right]=2\left[\left.\begin{matrix}(R)_2''\\(C_2H_5)_2\\(C_2H_5)_2\\(C_2H_5)H\end{matrix}\right\}N_2\right]I_2+\left[\left.\begin{matrix}(R)_2''\\(C_2H_5)_2\\H_2\\H_2\end{matrix}\right\}N_2\right]I_2$$

Treatment of these iodides with oxide of silver yields an alkaline solution containing the three bases in the hydrated state:—

$$(1.)\quad \left.\begin{matrix}\left[(R)_2''(C_2H_5)_2H_4N_2\right]''\\H_2\end{matrix}\right\}O_2$$

$$(2.)\quad \left.\begin{matrix}\left[(R)_2''(C_2H_5)_4H_2N_2\right]''\\H_2\end{matrix}\right\}O_2$$

$$(3.)\quad \left.\begin{matrix}\left[(R)_2''(C_2H_5)_5HN_2\right]''\\H_2\end{matrix}\right\}O_2$$

The first two (1 and 2), being capable of conversion into the volatile diamines,—

$$\left.\begin{matrix}(R)_2''\\(C_2H_5)_2\\H_2\end{matrix}\right\}N_2 \text{ and } \left.\begin{matrix}(R)_2'\\(C_2H_5)_2\\(C_2H_5)_2\end{matrix}\right\}N_2,$$

may be expelled from the solution by a current of steam, the non-volatile pentethylated diammonium compound being left behind.

1056. The pentethylated compound becomes converted into the di-iodide of the hexethylated diammonium, by further treatment with iodide of ethyl. *The formation of the pentethylated derivative establishes the diatomic character of the ammonia under examination.*

DIAMINES.

1057. The ideal type of this group is diammonia,—

$$\left.\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right\}N_2$$

The diamines may be subdivided, like the monamines, into three groups, viz.:—

Primary diamines.	Secondary diamines.	Tertiary diamines.
$\left.\begin{matrix}A_2\\H_2\\H_2\end{matrix}\right\}N_2$	$\left.\begin{matrix}A_2\\B_2\\H_2\end{matrix}\right\}N_2$	$\left.\begin{matrix}A_2\\B_2\\C_2\end{matrix}\right\}N_2$

1058. A broad line of demarcation appears in the chemical character of the diamines; for while some of them combine with two equivalents of acid, a great number combine, like the monamines, with only one equivalent. The capability of a diamine of uniting with one or two equivalents of an acid, must be intimately connected with the molecular construction of the basic system. As yet this connection remains unknown, and we are surprised to find this difference of saturating power in diammonic compounds, which, in every other respect, exhibit the greatest analogy.

1059. One of the most interesting groups of diamines is the class of bodies generally termed *ureas*, and of which urea, *par excellence*, furnishes the well-known prototype. They are interesting, not only because urea is found in the urine of men, and many other animals, and because it is one of the natural organic bodies which was earliest formed artificially, but also because such a variety of views have been adopted as regards its constitution.

1060. Urea is formed whenever cyanic acid or cyanates come in contact with ammonia, or ammoniacal salts. It is also formed by the spontaneous decomposition of an aqueous solution of cyanogen. Cyanate of ammonia is first formed, and this body becomes converted into urea as the liquid evaporates.

1061. Urea is now regarded as a diamine, two equivalents of hydrogen in diammonia being replaced by a diatomic radical, carbonyl. This view is supported both by its formation and products of decomposition. In the general view of polyammonias, we have shown that a diamine can be produced by bringing in contact with ammonia the chloride, iodide, or bromide of a diatomic radical. Now urea can be formed by acting upon ammonia with phosgene gas (bichloride of carbonyl), $COCl_2$; and the most characteristic transformation of urea is its decomposition into ammonia and carbonic acid, when it is submitted to the action of the alkalies. The formula of urea, viewed as a diammonium compound, is $\left.\begin{matrix}(CO)''\\H_2\\H_2\end{matrix}\right\}N_2$. In the place of the carbonyl, sulphcarbonyl (CS) can be substituted; we then get the following compound, $\left.\begin{matrix}CS\\H_4\end{matrix}\right\}N_2$, which is generally called sulphocyanide of ammonium. This body is formed, as is well known, by the direct union of ammonia and hydrosulphocyanic acid, as urea is by the direct action of ammonia on cyanic acid.

1062. The hydrogen in urea can be replaced by alcohol radicals; we then get compound ureas. The primary ones are obtained by the action of ammonia upon cyanic ethers:—

$$\underset{\text{Cyanic acid.}}{\left.\begin{matrix}(CO)''\\H\end{matrix}\right\}N} + H_3N = \underset{\text{Urea.}}{\left.\begin{matrix}(CO)''\\H_4\end{matrix}\right\}N_2}$$

$$\underset{\text{Cyanate of ethyl.}}{\left.\begin{matrix}(CO)''\\C_2H_5\end{matrix}\right\}N} + H_3N = \underset{\text{Ethyl-urea.}}{\left.\begin{matrix}(CO)''\\(C_2H_5)\\H_3\end{matrix}\right\}N_2}$$

The secondary ureas can be formed by acting upon the cyanic ethers with primary monamines, or by the action of water upon the cyanic ethers, thus:—

Diethyl-urea.

(1.)
$$\left.\begin{matrix}(CO)''\\ C_2H_5\end{matrix}\right\}N+\left.\begin{matrix}C_2H_5\\ H\\ H\end{matrix}\right\}N=\left.\begin{matrix}(CO)''\\ (C_2H_5)_2\\ H_2\end{matrix}\right\}N_2$$

(2.)
$$2\left(\left.\begin{matrix}(CO)''\\ (C_2H_5)\end{matrix}\right\}N\right)+\left.\begin{matrix}H\\ H\end{matrix}\right\}O=\left.\begin{matrix}(CO)''\\ (C_2H_5)_2\\ H_2\end{matrix}\right\}N_2+CO_2$$

1063. We must press upon the attention of the student that all bodies belonging to the class of bodies termed *ureas* must be formed in a manner corresponding to urea, and must experience, on being submitted to the action of the alkalies, corresponding decompositions. Before giving the student some exercises to work out, we will endeavour, by a few examples, to show how chemical philosophers frequently interpret, from the substances into which a body decomposes, the rational constitution of that body.

1st example.—Some years ago Hofmann obtained two bodies from aniline. One was best obtained by the action of phosgene gas on that substance, and the other was most abundantly procured by the action of bisulphide of carbon on aniline. These bodies might be viewed as diammonias in which two equivalents of hydrogen had been replaced by two of phenyl, and two other equivalents of hydrogen had been replaced, in one by the diatomic radical (C O)″, and in the other by the diatomic radical (C S)″. The rational formulæ of these bodies would therefore be,—

(1.) $\left.\begin{matrix}(CO)''\\ (C_6H_5)_2\\ H_2\end{matrix}\right\}N_2$, carbanilide, diphenyl-urea, or carbophenylamide.

(2.) $\left.\begin{matrix}(CS)''\\ (C_6H_5)_2\\ H_2\end{matrix}\right\}N_2$, sulphocarbanilide.

The two substances in question, as far as their formulæ are involved, obviously correspond to urea and sulphocyanide of ammonium. In their formation, likewise, they correspond to these bodies; but in their chemical nature they differ; for whilst urea exhibits the deportment of a base, and sulphocyanide of ammonium has a saline character, the two new bodies are perfectly indifferent substances.

1064. Nevertheless, to use Hofmann's words, "on considering the difference of the chemical properties of urea and sulphocyanide of ammonium, and on recollecting that the saline constitution of urea is much more hidden than that of sulphocyanide of ammonium, it appeared worth while to try whether the action of powerful agents would not reveal a similar, if I may use the term, saline construction in carbanilide and sulphocarbanilide. Experiment realized this anticipation.

1065. "In the conception of the above view, I have endeavoured to split the two bodies in question according to the equations—

$$\underset{\text{Carbanilide.}}{C_{13}H_{12}N_2O} = \underset{\text{Aniline.}}{C_6H_7N} + \underset{\text{Cyanate of phenyl.}}{C_7H_5NO}$$

and—

$$\underset{\text{Sulphocarbanilide.}}{C_{13}H_{12}N_2S} = C_6H_7N + \underset{\text{Sulphocyanide of phenyl.}}{C_7H_5NS}$$

suggested by analogous changes of urea and sulphocyanide of ammonium:—

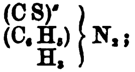
$$\underset{\text{Urea.}}{CH_4N_2O} = H_3N + \underset{\text{Cyanic acid.}}{CHNO}$$

$$\underset{\text{Sulphocyanide of ammonium.}}{CH_4N_2S} = H_3N + \underset{\text{Hydrosulphocyanic acid.}}{CHNS}$$

1066. "These reactions succeed without difficulty on submitting carbanilide and sulphocarbanilide to the action of agents capable of fixing aniline (anhydrous phosphoric acid, chloride of zinc, and even hydrochloric acid gas)."

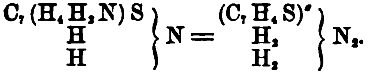
1067. 2nd example.—When benzonitrile is treated with a mixture of sulphuric and fuming nitric acid, it furnishes a solid nitro substitute, $C_7H_4(NO_2)N$. This body, under the influence of reducing agents (as sulphuretted hydrogen), undergoes the ordinary transformation of nitro compounds; an oily base is formed, which is represented by the formula, $C_7H_4(NH_2)N$. This base, when left in contact with sulphide of ammonium, is gradually changed into a well-defined base, which has this composition, $C_7H_8N_2S$. This new sulphuretted base has the same composition as a feebly basic body, sulphocarbonyl-phenyl-diamide, which Hofmann obtained by the action of ammonia on sulphocyanide of phenyl (the body which we have seen was formed in the decomposition of sulphocarbanilide).

1068. A comparison of the properties of the two bodies shows, however, that they are not identical; they are only isomeric; the constitution of the latter compound being represented by the expression,—



$$\left.\begin{matrix}(CS)''\\(C_6H_5)\\H_3\end{matrix}\right\}N_2;$$

whilst the constitution of the former may be expressed by the formula—



$$\left.\begin{matrix}C_7(H_4H_2N)S\\H\\H\end{matrix}\right\}N=\left.\begin{matrix}(C_7H_4S)''\\H_2\\H_2\end{matrix}\right\}N_2.$$

1069. Chancel obtained, by submitting nitrobenzamide to reducing agents, a base having the same composition as this new sulphuretted base, with the exception that it has oxygen in place of sulphur, $C_7H_8N_2O$. Hofmann obtained a body of exactly the same composition as Chancel's base by the action of vapour of cyanic acid upon aniline, or of ammonia with cyanate of phenyl,—

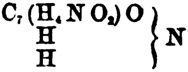
$$C_6H_7N + CHNO = C_7H_8N_2O$$

1070. Now although the formation of Hofmann's body showed it to be phenyl-urea, and the formation of Chancel's body showed it to be the amide of amido-benzoic acid,—

Benzamide . . . . . .

$$\left.\begin{matrix}C_7H_5O\\H\\H\end{matrix}\right\}N$$

Nitrobenzamide . . . .

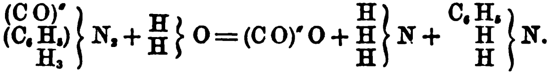


$$\left.\begin{matrix}C_7(H_4NO_2)O\\H\\H\end{matrix}\right\}N$$

Amidobenzamide . . .

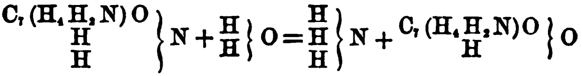
$$\left.\begin{matrix}C_7(H_4NH_2)O\\H\\H\end{matrix}\right\}N$$

still, as ordinary urea combines with acids, and as Chancel's compound combined with acids, and Hofmann's did not, chemists began to look upon Chancel's compound as the *true* phenyl-urea. Hofmann has called attention to the fact that compound ureas must resemble urea in their mode of formation, and in their products of decomposition. Now the body formed by Hofmann resembles urea in both these respects, whereas Chancel's compound does not conform to urea in either its formation or its decomposition. A compound urea, Hofmann states, when submitted to the action of alkalies, should yield, together with carbonic acid and ammonia, the monamine from which it has arisen. Phenyl-urea should therefore furnish carbonic acid, water, and phenylamine; and these are the products furnished by the body Hofmann formed by the action of cyanic acid on phenylamine.

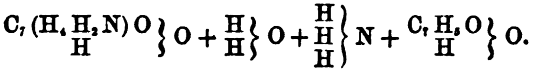


$$\left.\begin{matrix}(CO)''\\(C_6H_5)\\H_3\end{matrix}\right\}N_2+\left.\begin{matrix}H\\H\end{matrix}\right\}O=(CO)''O+\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N+\left.\begin{matrix}C_6H_5\\H\\H\end{matrix}\right\}N.$$

1071. In the formation of Chancel's compound, on the other hand, no cyanogen compound is involved, and it exhibits with potassa the deportment of an amidated amide. The reaction presents two distinct phases, ammonia and amido-benzoic acid being formed in the first place, and ammonia and benzoic acid in the second.



$$\left.\begin{matrix}C_7(H_4H_2N)O\\H\\H\end{matrix}\right\}N+\left.\begin{matrix}H\\H\end{matrix}\right\}O=\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N+\left.\begin{matrix}C_7(H_4H_2N)O\\H\end{matrix}\right\}O$$



$$\left.\begin{matrix}C_7(H_4H_2N)O\\H\end{matrix}\right\}O+\left.\begin{matrix}H\\H\end{matrix}\right\}O+\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N+\left.\begin{matrix}C_7H_5O\\H\end{matrix}\right\}O.$$

Hofmann's compound is therefore the true phenyl-urea.

EXERCISES.

183. Write out the formulæ for the following substances: — Sulphallyl-urea (thiosinamine), sulphethyl-allyl-urea, sulphophenyl-urea, methyl-urea.

184. Write out the formulæ for the following substances, state how you would prepare them, and into

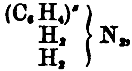
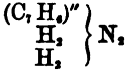
what substances they are decomposed by potash :—Allyl-urea, dimethyl-urea, diallyl-urea (sinapoline), ethyl-allyl-urea, ethyl-piperyl-urea.

1072. The ureas are all monacid.

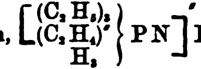
1073. The student is already aware (1024) that there are diamines in which a biatomic radical of the olefiant gas series occupies the place of two equivalents of hydrogen in one equivalent of the diamine.

EXERCISE.

185. Write out the formulæ, and state how you would prepare the following substances: — Ethylene-diamine, diethylene-diamine, ethylene-tetrethyl-diamine, ethylene-diethyl-diphenyl-diamine, ethylene-diphenyl-diamine.

1074. *Aromatic diamines.*—Hofmann has lately obtained, by the reduction of dinitrobenzole with acetate of iron, phenylene-diamine,  $\left.\begin{matrix}(C_6H_4)' \\ H_2 \\ H_2\end{matrix}\right\}N_2$, and he has examined a crystalline base from some aniline works, which proved to be toluylene-diamine,  $\left.\begin{matrix}(C_7H_6)'' \\ H_2 \\ H_2\end{matrix}\right\}N_2$. Toluol is almost invariably present in commercial benzole; and in the manufacture of aniline from nitrobenzole the dinitro-toluol becomes converted into toluylene-diamine. There are other basic bodies formed in the manufacture of aniline besides toluylene-diamine, one of which has been very recently examined by Hofmann; he finds it to be a diamine; from its composition ($C_{12}H_{14}N_2$), he has named it *paraniline*.

DIPHOSPHINES, DIARSINES, ETC.

1075. When dibromide of ethylene is made to act on triethyl-phosphine, two bromides (omitting the secondary products which are formed), are produced, viz., dibromide of ethylene-hexethyl-diphosphonium, and bromide of brom-ethyl-triethyl-phosphonium; the substances formed are therefore analogous to those which are produced when ethylene bromide acts upon triethylammonia. The dibromide is readily formed if the bromide of bromethyl-phosphonium is made to act upon the triethyl-phosphine. We can in this way obtain *onium* bodies in which we have two different members of the nitrogen group present. If we make bromide of bromethyl-triethyl-phosphonium act upon ammonia, the dibromide of ethylene-triethyl-phosphammonium,  $\left[\left.\begin{matrix}(C_2H_5)_3\\(C_2H_4)''\\H_3\end{matrix}\right\}PN\right]''Br_2$, is formed. If we make the bromethylated monatomic body act on ethylamine, we get a phosphammonium differently ethylated; when we make it act upon methylamine, we get a phosphammonium both ethylated and methylated. Now all these bromides of phosphammoniums, when treated with oxide of silver, yield hydrated oxides of phosphammoniums, which are powerful alkaline oxides.

1076. When bromide of bromethylated-triethyl-phosphonium is made to act upon triethylarsine, the two substances combine, dibromide of ethylene-hexethyl-phospharsonium being produced; this bromide, when treated with oxide of silver in *the cold*, yields hydrated oxide, of ethylene-hexethyl-phospharsonium. The phospharsonium compounds, and more especially the hydrated oxide are far less stable than the corresponding terms of the diphosphonium and even of the phosphammonium series.

1077. When bromide of bromethyl-triethyl-phosphonium is treated with oxide of silver, hydrated oxide of vinyl-triethyl-phosphonium is produced.

1078. When dibromide of ethylene is made to act upon triethylarsine, bromide of bromethyl-triethylarsonium is formed; this bromide, when treated with oxide of silver, yields hydrated oxide of vinyl-triethylarsonium.*

1079. When the bromide of bromethylarsonium is made to act upon triethylarsine, the dibromide of ethylene-hexethyl-diarsonium is formed. When this body is treated with oxide of silver, the hydrated oxide of ethylene-hexethyl-diarsonium is produced; this body is a powerful alkali.

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* Hofmann states that the bromide of bromethyl-triethyl-phosphonium, when treated with oxide of silver, is almost invariably converted into the oxethylated body (1081-2), its transformation into the vinyl compound being altogether exceptional. The bromide of the bromethylated arsonium, on the other hand, yields, as a rule, the vinyl body of the series, the formation of an oxethylated compound taking place only under particular circumstances; in fact, so rarely, as to leave some doubt regarding the existence of this term of the series.

1080. When bromide of bromethylated arsenium is made to act upon ammonia, the bibromide of ethylene-triethylarsammonium is produced. When this bromide is treated with oxide of silver, hydrated oxide of ethylene-triethylarsammonium is produced; this body is a stable caustic base.

1081. *Phosphoretted ureas.*—When sulphocyanide of phenyl, $\left(\left.\begin{matrix} CN \\ C_6H_5 \end{matrix}\right\} S\right)$, is brought into contact with triethyl-phosphine, they combine together in equivalent proportions; both the formation and deportment of this body show that it belongs to the class of bodies of which urea is the type; if urea be viewed as a monacid diamine, the rational composition of this body must be,—

$$\left.\begin{matrix} (CS)'' \\ (C_2H_5)_2 \\ (C_2H_5)(C_6H_5) \end{matrix}\right\} NP$$

It was the first example in which all the hydrogen in urea was removed by substitution. It is, like its prototype, a monacid base.

1082. When sulphocyanide of allyl is made to act upon triethyl-phosphine, a corresponding urea is formed. Hofmann has in vain endeavoured to produce, by the action of triethyl-phosphine on the sulphocyanides of methyl, ethyl, and amyl, compound ureas analogous to the allyl and phenyl bodies.

1083. Hofmann also endeavoured to obtain, by employing triethylarsine and triethyl-stibine in the place of triethyl-phosphine, the corresponding arsenetted and antimonetted ureas, but without success.

1084. Hofmann also endeavoured to obtain the corresponding oxygen ureas by employing cyanate of phenyl instead of sulphocyanide of phenyl, to act upon triethyl-phosphine, but without success.

DIAMIDES.

1085. The diamides are constructed on the type of two atoms of ammonia. They may be divided, like the monamides, into primary, secondary, and tertiary, according as one-third, two-thirds, or all the hydrogen is replaced by other radicals.

Primary diamides.	Secondary diamides.	Tertiary diamides.
$\left.\begin{matrix}A_2\\H_2\\H_2\end{matrix}\right\}N_2$	$\left.\begin{matrix}A_2\\B_2\\H_2\end{matrix}\right\}N_2$	$\left.\begin{matrix}A_2\\B_2\\C_2\end{matrix}\right\}N_2$

PRIMARY DIAMIDES.

1086. These bodies are formed by replacing two equivalents of hydrogen in diammonia, by one equivalent of a diatomic acid molecule.

1087. *Preparation.* 1st method.—They differ only from the neutral ammonium salts of the dibasic acids by two equivalents of water; they can, therefore, be prepared by merely distilling these salts.

Oxamide (oxalyl-biamide).

$$\left.\begin{matrix}(C_2O_2)''\\(H_4N)_2\end{matrix}\right\}O_2 - 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) = \left.\begin{matrix}(C_2O_2)''\\H_2\\H_2\end{matrix}\right\}N_2$$

2nd method.—They can also be prepared by treating the neutral ethers of the dibasic acids with an excess of ammonia.

$$\left.\begin{matrix}(C_2O_2)''\\(C_2H_5)_2\end{matrix}\right\}O_2 + 2\,H_3N = \left.\begin{matrix}(C_2O_2)''\\H_2\\H_2\end{matrix}\right\}N_2 + 2\left(\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O\right)$$

3rd method.—They have also been obtained by the action of ammonia on the diacid anhydrides.

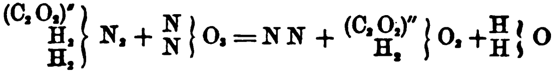
4th method.—"It is probable that the action of ammonia on diatomic chlorides, under appropriate circumstances, will also furnish them."

1088. Boiled with acids or alkalies, they fix the elements of water, and are resolved into ammonia and a bibasic acid.

$$\left.\begin{matrix}(C_2O_2)''\\H_2\\H_2\end{matrix}\right\}N_2 + 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) = \left.\begin{matrix}C_2O_2\\H_2\end{matrix}\right\}O_2 + 2\,H_3N$$

1089. Many of them, at an elevated temperature, evolve ammonia, and become transformed into secondary amides (imides).

1090. Under the influence of nitrous acid they disengage nitrogen, and are transformed into bibasic acids.



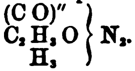
$$\left.\begin{matrix}(C_2O_2)''\\ H_2\\ H_2\end{matrix}\right\} N_2 + \left.\begin{matrix}N\\ N\end{matrix}\right\} O_3 = N\,N + \left.\begin{matrix}(C_2O_2)''\\ H_2\end{matrix}\right\} O_2 + \left.\begin{matrix}H\\ H\end{matrix}\right\} O$$

SECONDARY DIAMIDES.

1091. These bodies are obtained by the same processes as the primary diamides, employing monamines in the place of ammonia.

1092. When they are treated with acids or alkalies, they are decomposed into bibasic acids and monamines.

1093. The members forming the group of secondary monamides are viewed by some chemists as having double the formulæ there assigned them (1002); if this be the case, they would be secondary diamides.

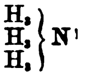
1094. When urea is treated with the chlorides of the monatomic acid radicals, it exchanges one equivalent of its hydrogen for one equivalent of the acid radical; by this exchange it becomes converted from a diamine into a diamide; these urea-amides hold an intermediate position between the primary and secondary amides,—Ex., acetyl-urea,  $\left.\begin{matrix}(C\,O)''\\ C_2H_3O\\ H_3\end{matrix}\right\} N_2$.

EXERCISE.[*]

186. Give the formulæ, and state how you would prepare the following substances: — Butyryl-urea, succinamide (succinyl-biamide), biethyloxamide (oxalyl-biethyl-biamide), valeryl-urea, oxalyl-biphenyl-biamide, malamide (asparagin), benzoyl-urea, biphenyl-malamide (malyl-diphenyl-biamide).

The student must now perform the following exercises —first exercise, 165 (p. 394); 2nd exercise, 152 (page 337). After he has gone through these exercises he commences the study of the tri- and tetra-amines.

TREBLE MOLECULE.



$$\left.\begin{matrix}H_3\\ H_3\\ H_3\end{matrix}\right\} N^1$$

TRIAMINES.

1095. We shall describe under the head of triamines not only those bodies, but also the triammonium compounds.

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[*] As the tertiary diamides are as yet little known, only a few members having been discovered, we shall pass them over without further notice.

1096. We have seen that for the production of an $(n + 1)$ atomic ammonia, n diatomic radicals are required, and that when $n = 2$ we must obtain the first term of a series of triammonium compounds.

1097. *Action of dibromide of ethylene on ammonia and ethylammonia.*—Dr. Hofmann, in the course of his researches, has ascertained that the volatile bases obtained by the action of dibromide of ethylene upon ammonia, consist, after several rectifications, almost exclusively of the two compounds, diethylene-triamine, and triethylene-triamine. These two amines, when separated from their salts by solid hydrate of potash, are in the anhydrous state, and appear as oily liquids; they are nearly colourless, and rapidly attract carbonic acid from the atmosphere. "It deserves to be noticed, that the tendency to form definite hydrates, so prominent in the diamines, is not met with in the case of the triamines." We have already noticed (1042) that the triammonias are capable of forming three classes of salts.

1098. Dr. Hofmann has found that by the action of dibromide of ethylene on ethylamine, both diatomic and triatomic bases are produced. Those boiling above 200° C. are two of the triamine series, containing, of course, both monatomic and diatomic radicals; these two bases are diethylene-triethyl-triamine, and triethylene-triethyl-triamine: these bases are oily liquids, powerfully caustic, extremely soluble in water; they boil between 220° and 250° C. He has also found that another triamine base is formed in the above reaction; this base is diethylene-diethyl-triamine.

1099. *Rosaniline.*—Beautiful colouring matters have, within the last few years, been obtained by treating aniline in various ways. These colouring matters are known to the public by the names of mauve, roseine, fuchsine, &c.

1100. To Mr. Perkins belongs the merit of first isolating and producing on a manufacturing scale that violet colour which aniline yields when treated with oxidizing agents, and which had been so often witnessed and employed as a test for aniline in scientific laboratories. Mr. Perkins took out a patent for this dye in 1856. He directs it to be prepared in the following way:—A cold solution of sulphate of aniline (rough aniline is used) and a cold solution of bichromate of potash are mixed together and left for ten or twelve hours. An abundant deposit of a black powder is thus obtained, which is separated, well washed with water, and, lastly, dried at 212° F. The dried substance is then digested several times with naphtha or commercial benzole, which dissolves a brown tarry or resinous substance, contaminating the colouring matter in the deposit. The residue insoluble in the naphtha is dried again, and then digested with wood spirit, or alcohol, or any other liquid able to dissolve the colouring matter. This clear solution is decanted and distilled to recover the solvent. The residue of the distillation is the mauve, or aniline violet. The composition of this substance does not appear to have been yet determined.

1101. In 1858, Dr. Hofmann contributed a paper to the Royal Society, entitled "Action of tetrachloride of carbon on aniline." In this paper Dr. Hofmann described a triamine he had formed by the action of the carbon chloride on aniline; this base he called carbo-triphenyl-triamine; he stated that the formation of this base was accompanied by that of a colouring matter of a magnificent crimson colour. Since that time this substance, which goes under the name of roseine, fuchsine, &c., has been produced on the manufacturing scale by the action of a variety of agents,—metallic chlorides, metallic nitrates, and numerous oxidizing agents,—on aniline.

1102. The composition of this substance has very recently been investigated by Dr. Hofmann, and as similar substances will, no doubt, be obtained from other bases allied to aniline, he proposes to commemorate the origin of the compound in its name; he accordingly proposes to name it *rosaniline*. Rosaniline is known to form two classes of salts, but it probably forms three classes, like other triamines. The two classes which it is known it forms are the monacid and the triacid salts. The monacid salts are exceedingly stable bodies, and they exhibit, for the most part, in reflected light, the splendid metal-lustrous green of the wings of the rose-beetle; in transmitted light the crystals are red, becoming opaque when they acquire certain dimensions. The solution of these salts in water or alcohol possesses the magnificent crimson colour for which rosaniline has become so celebrated. The salts with three equivalents of acid are comparatively instable, being decomposed by the action of water, or by exposure to 212°; they are yellowish brown in colour, both in the solid state and in solution. The monacid salts can be prepared either by the direct action of the respective acids, or by submitting the ammonium compounds of the several acids to ebullition with an excess of the free base. The formula for the monochloride is,—

$$C_{20}H_{19}N_3, HCl.$$

1103. The combustion of rosaniline led to the formula $C_{20}H_{19}N_3, H_2O$. This shows that the crystals which were submitted to analysis were the hydrate, as the salts of this base contain no oxygen. The crystallized hydrate, in its pure state, is absolutely white, but its solution in alcohol has a deep red colour; and even the crystals, when exposed to the action of the atmosphere, turn rapidly pink, and ultimately dark red, and no perceptible alteration of weight is observed during this change.

1104. When rosaniline is submitted to the action of reducing agents, such as nascent hydrogen, or sulphuretted hydrogen, it is readily attacked; a new base, which Hofmann has designated *leucaniline,* is formed. The formula of this new base is $C_{20}H_{21}N_3$; and the formula of its chloride is, when dried in vacuo, $C_{20}H_{21}N_3, 3HCl, H_2O$, showing that the chloride retains one equivalent of water. Leucaniline and its salts are white.

1105. Hofmann points out a very interesting relation between the two bases. In the anhydrous condition, the two bases hold to each other the relation which obtains between blue and white indigo.

Rosaniline - - - - -	$C_{20}H_{19}N_3$
Leucaniline - - - - -	$C_{20}H_{21}N_3$
Blue indigo - - - - -	$C_{16}H_{10}N_2O_2$
White indigo - - - -	$C_{16}H_{12}N_2O_2$

1106. Leucaniline is readily converted into rosaniline by oxidizing agents.

1107. We may observe, in conclusion, that the changes which accompany the formation of rosaniline from aniline are still unknown; but Dr. Hofmann states that in most of the processes which give rise to the rosaniline, it is accompanied by several other bases, the study of which he has not yet completed.

TRIPHOSPHONIUMS.

1108. We have noticed that the formation of the polyammonias may be accomplished in two essentially different ways; they are produced either by increasing in the same ratio the number of polyatomic radicals of given atomicity as the number of ammonia molecules you desire to coalesce (this was the plan the student will see Hofmann followed in producing the triamines), or by employing a radical of the atomicity which represents the number of ammonia molecules which it is desired to coalesce. Hofmann adopted this second plan to form the triphosphonium compounds.

1109. When iodoform is brought into contact with triethyl-phosphine, it fixes three equivalents of it, the tri-iodide of formyl-nonethyl-triphosphonium being formed. When this body is treated with oxide of silver, the trioxide is not produced, but it is split up into oxide of methyl-triethyl-monophosphonium, and the oxide of triethyl-phosphine.

EXERCISE.

187. Write out the formulæ of the following substances:—Trichloride of formyl-nonethyl-triphosphonium, diethylene-triamine, triethylene-triamine, diethylene-triethyl-triamine, triethylene-triethyl-triamine, diethylene-diethyl-triamine, monacetate of rosaniline, trinitrate of leucaniline, trinitrophenate of rosaniline, sulphate of rosaniline, oxalate of rosaniline.

TRIAMIDES.

1110. The triamides correspond to three molecules of ammonia, and, of course, they can be divided into primary, secondary, and tertiary bodies. But as very few triamides have yet been produced, we shall pass them over, just observing that cyanuric acid, when referred to the ammonia type, is a secondary triamide, and its ether is a tertiary one.

Cyanuric acid . . . . $\left.\begin{matrix}(CO)_3'' \\ H_3\end{matrix}\right\} N_3$

Cyanuric ether . . . . $\left.\begin{matrix}(CO)_3'' \\ (C_2H_5)_3\end{matrix}\right\} N_3$

QUADRUPLE MOLECULE.

$$\left.\begin{matrix}H_3\\H_3\\H_3\\H_3\end{matrix}\right\}N_4$$

1111. We shall here give a short outline of Hofmann's researches on the tetrammonium compounds. We have seen that for the production of an $(n+1)$ atomic ammonia, n diatomic radicals are required (1022); and the number of molecules of diatomic bromides, and the quantity of ammonia involved in the formation of these complex ammonias, is given in the general equation (1022). We have also shown that if $n=3$, we obtain a tetrammonium compound. In order to obtain the tetrammonium bodies, Hofmann first acted upon ammonia with dibromide of ethylene, but from the number of bases formed he was unable to obtain the tetrammonium compound pure; in his further researches he therefore employed diethylamine and ethylamine in place of ammonia. When dibromide of ethylene is made to act upon diethylamine in sealed tubes, the reaction is rapidly accomplished, both in the absence and presence of alcohol; three ammonium bromides are formed, viz., bromide of diethylammonium, dibromide of ethylene-tetrethyl-diammonium, and the tetrabromide of triethylene-octethyl-tetrammonium. The separation of these three salts presents no difficulties. Liberated by oxide of silver, and submitted to a protracted current of steam, the mixture of bases separates, on the one hand, into diethylamine and ethylene-tetrethyl-diamine, which pass over with the steam, and hydrate of triethylene-octethyl-tetrammonium, which remains behind. Hofmann submitted the free octethylated base to the action of iodide of ethyl. This treatment gave rise to a beautifully crystallized iodide, which was less soluble in alcohol than the free base just mentioned. This iodide was tetra-iodide of triethylene-non-ethyl-tetrammonium. He did not carry the ethylation any further.

1112. When dibromide of ethylene is made to act upon ethylamine, the reaction between these two bodies, as might have been expected from the number of unreplaced hydrogen equivalents in ethylamine, is far more complex than the action of the diatomic body upon diethylamine. The action is rapidly accomplished at 100° C., in sealed tubes. The crystalline mass which remains on evaporating the product to dryness, is a mixture of six, and occasionally of seven bromides, viz., bromide of ethylammonium, dibromide of ethylene-diethyl-diammonium, dibromide of diethylene-diethyl-diammonium, tribromide of diethylene-triethyl-triammonium, tribromide of triethylene-triethyl-triammonium, tetrabromide of pentethylene-tetrethyl-tetrammonium, tetrabromide of hexethylene-tetrethyl-tetrammonium. The ammonias corresponding to the first five of these bromides are all volatile; there is therefore no difficulty in separating them from the mixture liberated by means of oxide of silver; and submitted to the action of steam, they are carried over, and there is left behind a powerful alkaline liquor, which, in most cases, Hofmann found to consist exclusively of the hydrate of pentethylene-tetrethyl-tetrammonium. This compound contains still two equivalents of replaceable hydrogen. By the action of iodide of ethyl they may, Hofmann states, although with difficulty, be removed, and replaced by ethyl. He thus obtained successively the pentethylene-pent-ethylated, and lastly, the pentethylene-hexethylated tetrammonium.

1113. Hofmann finds that hexethylene-tetrethyl-tetrammonium may be obtained in a state of purity by the action of dibromide of ethylene upon ethylene-diethyl-diamine, and diethylene-diethyl-diamine.

1114. We have already noticed that Dr. Hofmann has proved that one of the products of the reaction of tetrachloride of carbon on triethyl-phosphine is tetrachloride of carbo-dodeca-ethyl-triphosphonium. For further information about the formation of this and the other product, and the substances into which they are decomposed by water, we must refer the student to the original memoir.*

EXERCISES.

188. What is the simplest tetrammonium compound

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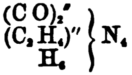
* "Action of triethyl-phosphine on the substitution compounds of marsh gas." By Dr. Hofmann. "Proceedings of Royal Society," vol. xi., No. 44.

which could possibly be formed by the action of a diatomic radical upon ammonia?

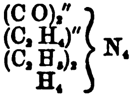
189. Write out the formulæ of the following bodies:—Tetrabromide of triethylene-octethyl-tetrammonium, the hydrate of triethylene octethyl-tetrammonium, the tetraiodide of triethylene-monethyl-tetrammonium, the hydrate of pentethylene-tetrethyl-tetrammonium, the tetrabromide of hexethylene-tetrethyl-tetrammonium, the hydrate of pentethylene-pentethylated tetrammonium, and the tetrachloride of pentethylene-hexethylated tetrammonium.

1115. Dr. Volhard has very recently succeeded in obtaining several ureas of the tetramine series. By acting upon the dichloride of ethylene-diammonium with cyanate of silver, he obtained a new crystalline substance, which he designates ethylene-urea. It has the following composition:—


$$\left.\begin{matrix}(CO)_2''\\(C_2H_4)''\\H_6\end{matrix}\right\}N_4 .$$

When boiled with a very concentrated solution of potassa, this body assimilates the elements of water, and splits into carbonic acid, ammonia, and ethylene-diamine.

1116. When cyanate of silver is treated with dibromide of ethylene-diethyl-diammonium, the diethylated urea is formed:—


$$\left.\begin{matrix}(CO)_2''\\(C_2H_4)''\\(C_2H_5)_2\\H_4\end{matrix}\right\}N_4 .$$

1117. "Cyanate of ethyl acts most energetically on ethylene-diamine. If the cyanate be poured into ethylene-diamine, each drop hisses like red-hot iron plunged into water. The mixture solidifies into a mass of needles, which, when recrystallized from water or spirit, furnish the new compound in a state of purity. The substance thus obtained presents the same composition as the product of the action of dibromide of ethylene-diethyl-diammonium on cyanate of silver, viz.:—

$$C_8H_{18}N_4O_2$$

1118. "The two ureas, however, are far from being identical. The urea obtained by combining cyanate of ethyl with ethylene-diamine is easily soluble in boiling water, difficultly soluble in cold water, even less soluble in spirit, and almost insoluble in absolute alcohol. It fuses without decomposition at 201°, solidifying again at 185°. This body is altogether indifferent. I did not succeed in obtaining a platinum salt or a gold salt of this urea, while the isomeric substance derived from ethylene-diethylamine furnishes both salts without difficulty.

1119. "The non-identity of the two bodies is thus sufficiently established, but the absolute difference in their construction is most conspicuously manifested in the products of decomposition which they yield under the influence of the alkalies. Treated with potash, the urea derived from ethylene-diethyl-diamine and cyanic acid, yields ethylene-diethyl-diamine and the products of decomposition of cyanic acid,—carbonic acid and ammonia. The urea, on the other hand, which is formed by the action of ethylene-diamine on cyanic ether, splits into ethylene-diamine, and the derivatives of cyanic ether, carbonic acid, and ethylamine.

1120. "It is thus evident that the two individual groups of elements, the union of which gives rise to the two different ethylated ethylene-ureas, remain as such, unaltered in these compounds."*

APPENDIX L.

1121. We must here inform the student that a great many important organic bodies, as the sugars, starches, gums, essential oils not containing oxygen, have not been noticed at all in any one of the last four chapters, although in these chapters organic bodies have been treated of to a considerable extent. The reason why they were omitted is this,—we cannot as yet refer them to any type. It is possible that the sugars may prove, like mannite, to be alcohols, but at present we have either no evidence, or not sufficient evidence, to refer these, or any of the other important bodies I have named, to any type.

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* Dr. Volhard "On the Ureas of the Diamines." "Proceedings of the Royal Society," vol. xi., No. 44.

1122. I have placed at the end of the book a series of questions on chemistry and chemical physics, which I have selected from the published examination papers of different examiners. I recommend the student to write out answers to the questions grouped under the head of chemistry, before he passes on to the next chapter.

CHAPTER XI.

OTHER VIEWS ON THE CONSTITUTION OF BODIES.

Wurtz's views, 1127. *Dr. Lyon Playfair's views,* 1136. *Dr. Frankland's views,* 1140. *Dr. Kolbe's views,* 1170. *Appendix M.*

1123. The student has already been made aware (pars. 529 to 533, and Appendix B, page 279) that, since the time Gerhardt and his followers first propounded the theory "that the molecules of all bodies occupy two volumes in the vapourous state," a number of facts have been discovered, which renders it imperative on chemists either to abandon that theory, or, if they continue to adopt it, to alter the atomic weights of a large number of the elements. Thus, in two gaseous volumes of the hydrides of the alcohol radicals, there are contained one atom of hydrogen and one of the compound radical. Now, as the metals have hitherto been considered the strict representatives of hydrogen, we should expect to find that in two volumes of the vapour of organo-metallic bodies there would be, as in the case of the hydrides, an equivalent of metal, and an equivalent of the alcohol radical; but this is not the case; in the two volumes of these bodies there are two equivalents of metal and two of the alcohol radicals. Nor is this difference between the condensation of hydrogen and the metals confined to organic compounds; it has been ascertained, from taking the vapour densities of various metallic chlorides, that the metals in various chlorides are in a more condensed form than the hydrogen in hydrochloric acid; therefore, if we admit that the molecules of all substances occupy two volumes in the gaseous state, and if the reasoning which has led chemists to double the atomic weight of oxygen be correct, the same reasoning must lead us to double the atomic weights of the greater number of the elements.

1124. These reasons have been very ably set forth by Dr. Wolcott Gibbs, in a paper which appeared in the *American Journal of Science:* this paper I have given almost in its entirety. That part of it which relates to the doubling of the atomic weights of other elements besides carbon, oxygen, and sulphur, is given in Appendix B, page 279. Since that part of my work was in print, a paper by Wurtz on the same subject has appeared in the *Journal of the Chemical Society of London;** the title of the paper is "On Oxide of Ethylene, considered as a link between Organic and Mineral Chemistry." The object of the paper is to prove that the present atomic weights of Ba, Sr, Ca, Mg, Mn, Fe, Zn, Cd, Cu, Pb, Hg, Sn, &c., ought to be doubled. He first proves that the new atomic weights accord better than any other with *the atomic heats of the elements*, with the *laws of isomorphism*, with the *vapour densities* of a great number of bodies; these physical proofs, with the exception of isomorphism, have been given in Gibbs' paper. He then adduces purely chemical proofs: he shows that the oxides of the metals, the atomic weights of which he proposes to double,—and if they are doubled, the metals become diatomic,—resemble in their chemical properties the oxide of the diatomic radical ethylene, he shows that they resemble oxide of ethylene in the formation of their hydrates, in the formation of their neutral and basic salts, in the formation of oxychlorides, oxyfluorides, in the formation of diammonium compounds, &c.; whereas, oxide of silver, and the oxides of the other metals which are considered monatomic, do not resemble oxide of ethylene, but resemble the oxides of the monatomic alcohol radicals in their chemical properties; therefore, as the oxides of Ba, Pb, Cu, &c., resemble in their chemical deportment the oxide of the diatomic radical ethylene, those metals must be diatomic, and, consequently, their atomic weights must be doubled.

1125. As Dr. Wolcott Gibbs did not adduce any reasons derived from the chemical deportment of the bodies for doubling their atomic weights, I have thought it necessary to place in a condensed form the paper of Wurtz before the student, as the question of atomic weights and the constitution of bodies is a most important one.

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* Vol. xv., p. 387.

1126. Dr. Lyon Playfair, Dr. Frankland, and Dr. Kolbe, have each proposed views on the constitution of bodies which differ from those adopted by Gerhardt and his followers: these views are brought before the student in the present chapter.

1127. *The views of Wurtz.*—Oxide of ethylene can displace magnesia, alumina, ferric oxide, and cupric oxide, from their acid combinations; it has, therefore, strong basic properties.

1128. Now, as the radical in oxide of ethylene is diatomic, the question arises, Are there any metallic oxides, the metals in which are diatomic? He considers that the atomic weights of Ba, Sr, Ca, Mg, Mn, Fe (ferrosum), Zn, Cu, Pb, Hg, &c., are double those which are commonly assigned to them, and therefore they become diatomic; consequently their oxides correspond, or are comparable with oxide of ethylene. The arguments which Wurtz adduces in support of the view that these metals have double the atomic weight usually assigned them, we will presently lay before the student; but we will first contrast the atomic weights of Berzelius, Gerhardt, and those proposed by Wurtz, for a few of the elements:—

Names of elements.	Atomic weights, referred to 1 of hydrogen.		
	Berzelius'.	Gerhardt's.	New.
Silicon	(44·4, ⅔ of which = 28)	28·	28·
Tin	117·6	58·75	118·
Barium	136·8	68·	136·8
Strontium	87·3	43·8	87 3
Calcium	40·2	20·	40·
Magnesium	25·	12	24·
Manganese	55·1	27·8	55·6
Iron	56·1	28·	56·
Zinc	65·	32·5	65·
Cadmium	111·4	55·7	111·4

Names of elements.	Atomic weights, referred to 1 of hydrogen.		
	Berzelius'.	Gerhardt's.	New.
Copper - -	63·3	31·5	63·
Lead - -	207·	103·5	207·
Mercury - -	200·2	100·	200·
Silver - -	215·6	108	108
Potassium -	78·3	39	39
Sodium - -	46·5	23	23
Lithium - -	13·	6·5	6·5

1129. For a considerable number of the metals, the new atomic weights and those of Berzelius correspond, being double those proposed by Gerhardt; therefore, the new formulæ for the oxides, &c., of these metals are identical with the old formulæ of Berzelius:* he wrote BaO; BaS; BaO, H_2O; $BaCl_2$; $BaSO_4$, &c. We return to these formulæ, but we agree with Gerhardt in writing K_2O; K_2S; KHO; KCl; K_2SO_4, &c.

1130. The new atomic weights correspond with those of Gerhardt for the metals Ag; K; Na; Li: these metals are monatomic, and, therefore, comparable with hydrogen.

1131. The new system of atomic weights accords better than any other with the physical data which serve to control the determination of the relative weights of the atoms. In fact, the numbers in the last column are identical with those designated by M. Regnault as "thermic equivalents." Thermic equivalents are fully considered in Chapter XIII; on that account we shall not now enter more fully upon the subject.

1132. In the next place, the new system of atomic weights is in harmony with the law of isomorphism, which requires that isomorphous bodies be represented by analogous formulæ. Thus, cuprous sulphide is isomorphous with sulphide of silver (see par. 265), and these two bodies have in the new system analogous formulæ, viz., Ag_2S and Cu_2S; whereas, by the formulæ assigned to them by Gerhardt, they had not an analogous composition; thus, Ag_2S, Cu_4S. Again, on the new system, the sulphates of silver and of sodium are represented by analogous formulæ, SAg_2O_4 and SNa_2O_4. The isomorphous sulphates of the magnesian series (see Group x., page 151) are expressed, in the new system, by the formulæ,—

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* See par. 277.

$$SMO_4 + 7H_2O.^*$$

And the composition of the double sulphates of the same series (see Group x.) is represented by the formula,—

$$SMO_4, SR_2O_4 + 6H_2O.$$

1133. The new atomic weights are in harmony with the vapour densities of a very considerable number of bodies. The exceptions observed relate to the vapour densities of certain elementary bodies. Thus the atomic weights of phosphorus, arsenic, mercury, zinc, and cadmium, calculated from their vapour densities, do not agree with those which are deduced from other considerations.† But these cases may be regarded as exceptional, as the vapour densities of the larger number of the compounds into

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* A large number of salts contain quantities of water, which, in Gerhardt's notation, must be represented by a fractional number of molecules ($H_2O = 18$). Now this inconvenience is obviated if we double the atomic weights of a certain number of the metals. We select one out of many examples:—

Gerhardt's notation.	New notation.
$NiCl + 4\frac{1}{2}H_2O$	$Ni^{\prime\prime}Cl_2 + 9H_2O.$

† The atomic weights of the elementary bodies (referred to one volume) are obtained by multiplying their vapour densities by $14{\cdot}44 = \frac{1}{0{\cdot}0693}$; and the molecular weights (referred to two volumes) are obtained by multiplying the vapour densities by $28{\cdot}88 = \frac{1}{0{\cdot}03463}$. But on multiplying the vapour densities of mercury (6·976) and of cadmium (3·94) by 28·88, we find the numbers 201·4 and 113·7; and the anomaly exhibited by these metals may be expressed by saying that their molecular weights, such as are deduced from their vapour densities, really represent their atomic weights (200 = Hg; 111·5 = Cd). On the other hand, if we multiply the vapour densities of phosphorus (4·42) and of arsenic (10·6) by 14·44, we obtain the numbers 63·8 and 153, an anomaly which may be expressed by saying that the atomic weights of these bodies, as deduced from their vapour densities, really express their molecular weights (P,P = 63; As As = 150).—(*Wurtz.*) The specific gravity of several of the polyatomic elements, and also, as we have noticed, of the diatomic radicals of the ethylene family, is only one-half that of their atomic weights; they therefore resemble compound bodies in this respect (see par. 120). They do not appear to conform to the same law as monatomic, elementary, and compound radicals, and which Gerhardt applied both to polyatomic and monatomic radicals; for their elements in the free state do not appear to be united in pairs, like the monatomic elements; consequently their combining atom and their molecular atom must be the same.—R. G.

which these elements enter are in accordance with their atomic weights.*

1134. If we adopt the new atomic weights, and thus render the metals we have named diatomic, oxide of ethylene becomes the analogue of these oxides; as oxide of ethyl is the analogue of the oxides of the monatomic metals, and oxide of glyceryl is the analogue of the teratomic metals. Examples:—

$$\left.\begin{matrix}Ag'\\Ag'\end{matrix}\right\}O \qquad Ba''O \qquad \left.\begin{matrix}Sb'''\\Sb'''\end{matrix}\right\}O_3$$

$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O \qquad C_2H_4''O \qquad \left.\begin{matrix}C_3H_5'''\\C_3H_5'''\end{matrix}\right\}O_3$$

1135. We will now contrast the chemical deportment of oxide of ethylene with the chemical deportment of the oxides of these diatomic metals.

1st. Oxide of barium is capable of combining with oxygen, and forming with it a binoxide. Oxide of ethylene is also capable of combining with oxygen, but the combination takes place under different conditions to that of $Ba''O$ and O, and the compound produced is acid, and not neutral, like binoxide of barium. The oxidation of oxide of ethylene takes place in contact with platinum black; the compound formed is glycolic acid. Glyoxylic acid may be regarded as a still higher oxide. We may therefore construct the following series:—

C_2H_4	ethylene
C_2H_4O	oxide ethylene
$C_2H_4O_2$	glycolic acid
$C_2H_4O_3$	glyoxylic acid

There are other series of the same kind in organic chemistry, and there are also similar series in mineral chemistry, as shown by the following examples:—

ClH	PH_3
$ClHO$	PH_3O_2
$ClHO_2$	PH_3O_3
$ClHO_3$	PH_3O_4
$ClHO_4$	

---

* See Appendix B. 1, page 280.

2nd. Oxide of barium unites directly with water, forming hydrate of baryta. Oxide of ethylene, in like manner, is capable of fixing water, glycol (hydrated oxide of ethylene) being produced. There is a parallelism between the hydrated oxides of the compound radicals in organic chemistry, and the hydrated oxides of the metals. Examples:—

Potassa.	Baryta.	Antimonic hydrate.	Ferric hydrate.
$\left.\begin{matrix}K\\H\end{matrix}\right\}O$	$\left.\begin{matrix}Ba''\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}Sb'''\\H_3\end{matrix}\right\}O_3$	$\left.\begin{matrix}{}^{*}Ffe^{vi}\\H_6\end{matrix}\right\}O_6$
Vinic alcohol.	**Glycol.**	**Glycerin.**	**Hexylic hydrate† (mannite).**
$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$	$\left.\begin{matrix}(C_2H_4)''\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3$	$\left.\begin{matrix}(C_6H_8)^{vi}\\H_6\end{matrix}\right\}O_6$

Not only can *one*, but even *two, three, four, five,* or more molecules of oxide of ethylene can combine with *one* molecule of water, these more complex hydrates forming the polyethylenic alcohols, which have already been noticed (page 348). They may be regarded as resulting from the partial dehydration of an increasing number of molecules of glycol:—

Diethylenic alcohol.

$$2\left(\left.\begin{matrix}C_2H_4\\H_2\end{matrix}\right\}O_2\right)-H_2O=\left.\begin{matrix}C_2H_4\\C_2H_4\\H_2\end{matrix}\right\}O_3$$

Triethylenic alcohol.

$$3\left(\left.\begin{matrix}C_2H_4\\H_2\end{matrix}\right\}O_2\right)-2H_2O=\left.\begin{matrix}C_2H_4\\C_2H_4\\C_2H_4\\H_2\end{matrix}\right\}O_4$$

Tetrethylenic alcohol.

$$4\left(\left.\begin{matrix}C_2H_4\\H_2\end{matrix}\right\}O_2\right)-3H_2O=\left.\begin{matrix}C_2H_4\\C_2H_4\\C_2H_4\\C_2H_4\\H_2\end{matrix}\right\}O_5$$

This property of accumulating in combination is not peculiar to ethylene. Amongst the organic radicals, acetyl and glyceryl have already been found to possess it: of the compound radicals in mineral chemistry, *sulphuryl*, *chromyl*, and *phosphoryl* possess the property. Examples:—

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* $Ffe = Fe_4 = 112$.

† See par. 561.

Nordhausen sulphuric acid.	Chromate of potash.	Pyrophosphoric acid.
$\left.\begin{matrix} SO_2 \\ SO_2 \\ H_2 \end{matrix}\right\} O_3$	$\left.\begin{matrix} CrO_2 \\ CrO_2 \\ K_2 \end{matrix}\right\} O_3$	$\left.\begin{matrix} (PO)''' \\ (PO)''' \\ H_4 \end{matrix}\right\} O_5$

Of the elementary bodies which possess the property of accumulating a number of atoms in one and the same molecule, Wurtz selects tin and silicon, both tetratomic elements.

The formula for *stannic hydrate* is $\left.\begin{matrix} Sn^{iv} \\ H_4 \end{matrix}\right\} O_4$. It loses, when dried *in vacuo*, an atom of H_2O, and is thus changed into a hydrate of this composition, $\left.\begin{matrix} Sn^{iv} \\ H_2 \end{matrix}\right\} O_3$. The formula for metastannic hydrate is, according to Fremy, $\left.\begin{matrix} 5\,Sn^{iv} \\ H_{20} \end{matrix}\right\} O_{20}$. At 100° C. it gives off one-half its water, and by this loss becomes converted into a hydrate having this formula, $\left.\begin{matrix} 5\,Sn^{iv} \\ H_{10} \end{matrix}\right\} O_{15}$.

In the following table of silicic acid, the formulæ ranged on the same horizontal line afford examples of continually-increasing condensation, whilst those in the same vertical column represent the hydrates, or rather anhydrides, formed successively by the loss of a continually-increasing number of molecules of water.

$\left.\begin{matrix} Si \\ H_4 \end{matrix}\right\} O_4$	$\left.\begin{matrix} Si \\ Si \\ H_8 \end{matrix}\right\} O_8$	$\left.\begin{matrix} Si \\ Si \\ Si \\ H_{12} \end{matrix}\right\} O_{12}$	$\left.\begin{matrix} Si_4 \\ H_{16} \end{matrix}\right\} O_{16}$	„	$\left.\begin{matrix} Si_6 \\ H_{24} \end{matrix}\right\} O_{24}$
$\left.\begin{matrix} Si \\ H_2 \end{matrix}\right\} O_3$	$\left.\begin{matrix} Si_2 \\ H_6 \end{matrix}\right\} O_7$	$\left.\begin{matrix} Si_3 \\ H_{10} \end{matrix}\right\} O_{11}$	$\left.\begin{matrix} Si_4 \\ H_{14} \end{matrix}\right\} O_{15}$	„	„
	$\left.\begin{matrix} Si_2 \\ H_4 \end{matrix}\right\} O_6$	$\left.\begin{matrix} Si_3 \\ H_8 \end{matrix}\right\} O_{10}$	$\left.\begin{matrix} Si_4 \\ H_{12} \end{matrix}\right\} O_{14}$	„	„
	$\left.\begin{matrix} Si_2 \\ H_2 \end{matrix}\right\} O_5$	$\left.\begin{matrix} Si_3 \\ H_6 \end{matrix}\right\} O_9$	$\left.\begin{matrix} Si_4 \\ H_{10} \end{matrix}\right\} O_{13}$	„	„

$$\left.\begin{matrix}Si_3\\H_4\end{matrix}\right\}O_8 \quad \left.\begin{matrix}Si_4\\H_8\end{matrix}\right\}O_{12} \quad ,, \quad ,,$$

$$\left.\begin{matrix}Si_3\\H_2\end{matrix}\right\}O_7 \quad \left.\begin{matrix}Si_4\\H_6\end{matrix}\right\}O_{11} \quad ,, \quad \left.\begin{matrix}Si_6\\H_8\end{matrix}\right\}O_{16}*$$

Normal silicic ether.	Okenite.	Ryacolite.	Leucite.	Felspar (orthoclase).
$\left.\begin{matrix}Si\\(C_2H_5)_4\end{matrix}\right\}O_4$	$\left.\begin{matrix}Si_2\\Ca''\\H_4\end{matrix}\right\}O_7$	$\left.\begin{matrix}Si_3\\\dagger All^{vi}\\2M'\end{matrix}\right\}O_{10}$	$\left.\begin{matrix}Si_4\\All^{vi}\\2M'\end{matrix}\right\}O_{12}$	$\left.\begin{matrix}Si_6\\All^{vi}\\K_2\end{matrix}\right\}O_{16}$

Olivine.	Diopside.
$\left.\begin{matrix}Si\\2Mg''\end{matrix}\right\}O_4$	$\left.\begin{matrix}Si\\Ca''\\Mg''\end{matrix}\right\}O_6$

Diethylic silicate.	Diethylic disilicate.
$\left.\begin{matrix}Si\\(C_2H_5)_2\end{matrix}\right\}O_3$	$\left.\begin{matrix}Si_2\\(C_2H_5)_2\end{matrix}\right\}O_5$

We see, then, that this theory enables us to conceive, and even to predict, the existence of a very large number of silicates, and that it was not without reason that these compounds have received the epithet *polysilicic*. Their constitution, and the formulæ which represent them, are not always very simple, and cannot be so in a great number of cases; but that which is really simple and rational is their mode of generation, based on the principle of the *accumulation of polyatomic radicals*.

3rd. Oxide of ethylene combines directly with acids, forming salts (ethylenic ethers). We have already noticed that it can combine with one or two atoms of acetic acid; when it is heated along with acetic anhydride, the diacetate is produced. It resembles oxide of lead in this capability of combining with one or two atoms of acetic acid:—

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[*] These compounds of tin and silicon do not appear to me to be parallel examples with those of the polyethylenic bodies. If we examine the formulæ of the silicon compounds ranged on the same horizontal line, we see it is doubling or trebling, &c., of the entire hydrated molecule, not of the oxide of silicon; or, if we take the vertical column, the hydrogen and oxygen decrease, whilst the quantity of silicon remains constant: whereas, in the polyethylenic it is oxide of ethylene which accumulates; the quantity of hydrogen remains constant, but the quantity of ethylene and oxygen increases.—R. G.

[†] $All = Al_4 = 54{\cdot}8$.

Monacetate of ethylene.

$$\left.\begin{matrix}(C_2H_4)' \\ C_2H_3O \\ H\end{matrix}\right\} O_2$$

(So called) Bibasic acetate of lead.

$$\left.\begin{matrix}Pb' \\ C_2H_3O \\ H\end{matrix}\right\} O_2 + H_2O$$

Diacetate of ethylene.

$$\left.\begin{matrix}(C_2H_4)' \\ (C_2H_3O)_2\end{matrix}\right\} O_2$$

Dicetate of lead (sugar of lead).

$$\left.\begin{matrix}Pb'' \\ (C_2H_3O)_2\end{matrix}\right\} O_2 + 3\ H_2O$$

But the analogy between oxide of ethylene and the oxide of lead, and also the oxide of copper, does not end here. There are basic salts of lead and copper; that is, several molecules of oxide of lead or oxide of copper can unite with acetic and other acids, and there are basic salts of oxide of ethylene, for polyethylenic acetates are salts of this description.

Diethylenic acetate.

$$\left.\begin{matrix}(C_2H_4)' \\ (C_2H_4)' \\ (C_2H_3O)_2\end{matrix}\right\} O_3$$

Dicupric acetate.

$$\left.\begin{matrix}Cu' \\ Cu' \\ (C_2H_3O)_2\end{matrix}\right\} O_3 + 3\,H_2O$$

Nitroso-nitrate of lead.

$$\left.\begin{matrix}Pb' \\ Pb' \\ NO \\ NO_2\end{matrix}\right\} O_3$$

Triethylenic acetate.

$$\left.\begin{matrix}(C_2H_4)''_3 \\ (C_2H_3O)_2\end{matrix}\right\} O_4$$

Tricupric acetate.

$$\left.\begin{matrix}Cu_3' \\ (C_2H_3O)_2\end{matrix}\right\} O_4$$

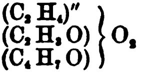
Triplumbic acetate.

$$\left.\begin{matrix}Pb' \\ (C_2H_3O)_2\end{matrix}\right\} O_4 + 3\,H_2O$$

These basic salts owe their existence and formation to the tendency possessed by polyatomic radicals, both simple and compound, of accumulating in combinations. We are not acquainted with any well-defined basic salts formed by the union of monobasic acids with oxides of potassium, sodium, lithium, and silver; and the power of forming basic salts, possessed by most other oxides, may, perhaps, be altogether dependent on the polyatomic nature of their metallic radicals. The following facts, however, exhibit this polyatomicity in a still clearer light.

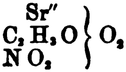
We have already noticed that the two atoms of acid with which oxide of ethylene is capable of uniting, can be two different acid radicals; there have also been formed salts of the oxides of the diatomic metals barium and strontium, in which the two atoms of acid are different; in this respect, therefore, oxide ethylene and the oxides of barium and strontium correspond.

Aceto-butyric glycol.



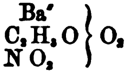
$$\left.\begin{matrix}(C_2H_4)''\\(C_2H_3O)\\(C_4H_7O)\end{matrix}\right\}O_2$$

Nitro-acetate of strontium.



$$\left.\begin{matrix}Sr''\\C_2H_3O\\NO_2\end{matrix}\right\}O_2$$

Nitro-acetate of barium.

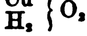


$$\left.\begin{matrix}Ba'\\C_2H_3O\\NO_2\end{matrix}\right\}O_2$$

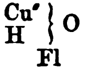
In these compounds, the diatomic radicals—ethylene, strontium, and barium—perform exactly the same functions as the diatomic radical of tartaric acid in Rochelle salt; and the existence of the aceto-nitrate of strontium, and the similar salt of barium, affords as strong an argument in favour of the double atomic weight of these metals, as that which was deduced by Liebig from the existence of Rochelle salt, for doubling the formula of tartaric acid.

4th. Oxide of ethylene unites directly with hydrochloric acid, forming monochlorhydric glycol, $\left.\begin{matrix}C_2H_4\\H\\Cl\end{matrix}\right\}O$: we know no metallic monochlorhydrins, but a sulphuric monochlorhydrin, $\underset{Cl}{\left.\begin{matrix}SO_2\\H\end{matrix}\right\}}O_2$, is known; and there are several well-defined fluorhydrins (oxyfluorides) known. Crystallized oxyfluoride of copper, the formula of which is, if we adopt the old atomic weights, $Cu\,Fl, Cu\,O, H\,O$, becomes, if we adopt the new atomic weights for oxygen and copper, $Cu'O, H\,Fl$: this compound stands in the same relation to cupric hydrate as monochlorhydric glycol to glycol.

Cupric hydrate.

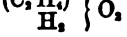


$$\left.\begin{matrix}Cu'\\H_2\end{matrix}\right\}O_2$$

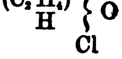


$$\underset{Fl}{\left.\begin{matrix}Cu'\\H\end{matrix}\right\}}O$$

Glycol.



$$\left.\begin{matrix}(C_2H_4)'\\H_2\end{matrix}\right\}O_2$$



$$\underset{Cl}{\left.\begin{matrix}(C_2H_4)'\\H\end{matrix}\right\}}O$$

The polyethylenic alcohols form chlorhydrins; and Rose has described a compound of hydrate of lime and chloride of calcium, to which he has assigned the following formula, $3\,CaO, CaCl + 16\,HO$; employing the new atomic weights, this formula becomes $3\,Ca'O, Ca'Cl_2$ $16\,H_2O$, and may be written as follows:—

Dichlorhydrin of tetrethylenic alcohol.

$$\begin{matrix}\left.\begin{matrix}Ca\\Ca\\Ca\\Ca\end{matrix}\right\}O_3 + 16\,H_2O,\ \text{which is analogous to}\ \left.\begin{matrix}C_2H_4\\C_2H_4\\C_2H_4\\C_2H_4\end{matrix}\right\}O_3\\ Cl_2 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad Cl_2\end{matrix}$$

Oxychloride of lead, $2\,PbO, PbCl_2$, and oxychloride of copper, $3\,CuO, Cl\,Cl_2$, possess an analogous constitution.

The typical hydrogen in monochlorhydrin can be replaced by an acid radical. Dr. Simpson has formed, for instance, aceto-chlorhydric glycol, which may be formulated thus, $\begin{matrix}\left.\begin{matrix}(C_2H_4)''\\(C_2H_3O)\end{matrix}\right\}O\\ Cl\end{matrix}$; or, more simply, thus, $\left.\begin{matrix}(C_2H_4)'\\(C_2H_3O)\end{matrix}\right\}\begin{matrix}O\\Cl.\end{matrix}$ There are certain mineral compounds of analogous constitution, excepting that in place of acetyl they contain polybasic radicals. Thus, *Wagnerite* and *Apatite*, which are well-characterised mineral species, are fluophosphates of magnesium and calcium, to which may be assigned the formulæ,—

$$PO_5\,3\,MgO + MgFl \text{ and } 3\,(PO_5, 3\,CaO) + CaFl,$$

which, in the new notation, become—

$$\left.\begin{matrix}(PO)'''\\2\,Mg'\end{matrix}\right\}\begin{matrix}O_3\\Fl\end{matrix} \text{ and } \left.\begin{matrix}3\,(PO)'''\\5\,Ca'\end{matrix}\right\}\begin{matrix}O_9\\Fl\end{matrix}$$

Wagnerite and apatite are, in fact, the phosphofluorhydrins of the hydrates,—

$$\left.\begin{matrix}(PO)'''\\H_5\end{matrix}\right\}O_4 \text{ and } \left.\begin{matrix}(PO)_3'''\\H_{11}\end{matrix}\right\}O_{10}$$

And here, Wurtz observes, we have occasion for an important remark. Ordinary phosphoric acid, $\left.\begin{matrix}(PO)'''\\H_3\end{matrix}\right\}O_3$, requires, to saturate it, more than one atom of magnesium ($Mg' = 24$); but two atoms of this magnesium, which are equivalent to four atoms of hydrogen, are too much for the purpose; it would therefore be supersaturated if the fourth combining unit of the group $2\,Mg'$, were not saturated by the fluorine. The same reasoning applies to apatite and the calcium contained in it. We see, therefore, that in these compounds, whose constitution appears so strange when regarded from the dualistic point of view, the fluorine or the chlorine plays an important and necessary part. I may add, that the presence of such a monatomic element in these compounds furnishes an argument in favour of the diatomicity of magnesium and of calcium. If magnesium were monatomic, the fluorine would be useless, for 3 Mg (Mg = 12) could replace 3 H in ordinary phosphoric acid. But the magnesium or calcium being diatomic, and, therefore, of even atomicity, the presence of a monatomic element becomes necessary to fill up the uneven atomicity of the phosphoryl $(PO)'''$.[*] Other compounds may likewise be regarded from this point of view.

5th. We have already seen that one atom of ethylene and two atoms of ammonium unite together, forming ethylene-diammonium. Now cupric ammoniums are known, and they have had the following formulæ assigned, thus:—

$$\begin{array}{ccc} \text{Cupriconium.} & & \text{Amicupriconium.} \\ N\left\{\begin{array}{l} Cu \\ H \\ H \\ H \end{array}\right. & \text{and} & N\left\{\begin{array}{l} Cu \\ Am \\ H \\ H \end{array}\right. \end{array}$$

Now if we admit that copper is a diatomic metal, these formulæ must be doubled, and then they become analogous in composition to ethlyene-diammonium, thus:—

$$\begin{array}{cccc} \text{Ethylene-diammonium.} & \text{Cupriconium.} & \text{Diami-cupriconium.} & \text{Tetrami-cupriconium.} \\ N_2\left\{\begin{array}{r} (C_2H_4)'' \\ H_2 \\ H_2 \\ H_2 \end{array}\right. & N_2\left\{\begin{array}{l} Cu'' \\ H_2 \\ H_2 \\ H_2 \end{array}\right. & N_2\left\{\begin{array}{l} Cu'' \\ Am_2 \\ H_2 \\ H_2 \end{array}\right. & N_2\left\{\begin{array}{l} Cu'' \\ Am_2' \\ Am_2 \\ H_2 \end{array}\right. \end{array}$$

Oxide of ethylene also enters into direct combination with ammonia, forming another class of bases, called *oxyethylenic.* Wurtz considers the base obtained by Millon, by the action of ammonia on mercuric oxide, as analogous to the oxyethylenic bases.

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[*] M. Cannizzaro adduces another chemical argument in favour of the diatomicity of calcium and barium, namely, that whereas there exists a quadroxalate of potassium, we are not acquainted with a quadroxalate of calcium or barium. In fact, a single atom of hydrogen in two molecules of oxalic acid may be replaced by an atom of potassium, but not by an atom of diatomic calcium, which is equivalent to two atoms of hydrogen. If, then, a portion of the hydrogen in two molecules of oxalic acid is replaced by calcium or barium, the result of the substitution can only be a binoxalate.

1136. *Dr. Lyon Playfair's views.*[*]—According to the views of Gerhardt and his followers, a salt is constituted on the type of water, $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$, in which, sometimes, an electro-positive body, like potassium, may substitute one equivalent of hydrogen; while an electro-negative radical may substitute the other equivalent, as in the case of sulphate of potash, $\left.\begin{matrix}K\\SO_3\end{matrix}\right\}O_2$, or nitrate of soda, $\left.\begin{matrix}Na\\NO_4\end{matrix}\right\}O_2$. These electro-negative radicals are assumed to exist in these salts, and in the hydrated acids which constitute them, and in many cases are not known in a separate state. Dr. Lyon Playfair, in a communication which he made to the British Association at Oxford, at its last meeting there, proposed another view of the constitution of neutral salts. It is to be observed that on the water type, neutral salts are supposed to be constructed on a type of the most highly basic oxides, such as potash, $\left.\begin{matrix}K\\K\end{matrix}\right\}O_2$. The oxide selected by Dr. Playfair for the type of neutral salts, is the neutral peroxide, MO_2, such as peroxide of hydrogen, $\left.\begin{matrix}O\\O\end{matrix}\right\}H$, or peroxide of manganese, $\left.\begin{matrix}O\\O\end{matrix}\right\}Mn$, oxides which are neither basic nor acid, except in a few cases, such as sulphurous acid and carbonic acid, where the element uniting with oxygen is either strongly electro-negative in itself, or feebly so. In forming a neutral salt, this chemist supposes that part of the electro-negative oxygen may be replaced by the well-known electro-negative anhydrides, and that the electro-positive hydrogen may be replaced by an electro-positive basyl. According to this view, the above salts would be written on the type peroxide of hydrogen, $\left.\begin{matrix}O\\O\end{matrix}\right\}H$, and nitric acid becomes $\left.\begin{matrix}O\\NO_5\end{matrix}\right\}H$; while nitrate of potash is $\left.\begin{matrix}O\\NO_5\end{matrix}\right\}K$. He also conceives that hydrates are true salts, hydrate of potash being $\left.\begin{matrix}O\\HO\end{matrix}\right\}K$; and it follows from this view that the molecules of free protoxides are also M O, M O, like a peroxide, M O, O. In support of this view, it is necessary that decompositions should be at least as simply expressed by it as by the former view, and that there should be instances shown in which oxygen may replace an acid in a salt, and where an acid may replace oxygen in an oxide. As an example of oxygen substituting an acid in a salt, we have the reaction used by bleachers in recovering oxide of manganese, after making chlorine. They convert the chloride of manganese into a carbonate, and heating it in air, substitute by oxygen all the carbonic acid.

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[*] Drs. Playfair, Frankland, and Kolbe each employ the old atomic weights. Drs. Frankland and Kolbe double the atom of carbonic acid and sulphuric acid.

$$\left.\begin{matrix}O\\CO_2\end{matrix}\right\}Mn + O = \left.\begin{matrix}O\\O\end{matrix}\right\}Mn + CO_2$$

We see a similar action when minium is made by roasting carbonate of lead in the air. The converse of this action, or the substitution of O by an acid, is familiar.

$$\left.\begin{matrix}O\\O\end{matrix}\right\}Mn + SO_3 = \left.\begin{matrix}O\\SO_3\end{matrix}\right\}Mn + O$$

Bearing in mind that, according to this view, hydrates and salts are constituted on the type of a peroxide, such as $\left.\begin{matrix}O\\O\end{matrix}\right\}Ba$, the following equations of the action of acids, oxygen, and water on barytes, are remarkably simple.

(1.) $\left.\begin{matrix}O\\O\end{matrix}\right\}Ba + CO_2 = \left.\begin{matrix}O\\CO_2\end{matrix}\right\}Ba + O$, in which an acid substitutes oxygen.

(2.) $\left.\begin{matrix}O\\O\end{matrix}\right\}Ba + HO = \left.\begin{matrix}O\\HO\end{matrix}\right\}Ba + O$, in which water substitutes oxygen.

(3.) $\left.\begin{matrix}O\\HO\end{matrix}\right\}Ba + O = \left.\begin{matrix}O\\O\end{matrix}\right\}Ba + HO$, in which oxygen substitutes water.

(4.) $\left.\begin{matrix}O\\HO\end{matrix}\right\}Ba + CO_2 = \left.\begin{matrix}O\\CO_2\end{matrix}\right\}Ba + HO$, in which an acid substitutes water.

1137. The two reactions in which oxygen decomposes hydrate of barytes, forming peroxide of barium, and in which steam decomposes the latter, with the re-formation of hydrate of barytes, form the patented process for making oxygen on a large scale. The same action is seen in dissolving peroxide of potassium in water, and in acting upon peroxide of sodium with carbonic acid.

$$K\,O_4 + 2\,H\,O = (K\,O_2,\ 2\,H\,O) + 2\,O$$
$$Na\,O_2 + C\,O_2 = Na\,O,\ C\,O_2 + O$$

In the burning of limestone, vapour of water is necessary to drive out the acid, from a similar chemical reason, and not, as generally ascribed, to diffusion. If these views of Dr. Playfair's be well grounded, we ought to have instances in which part of the oxygen of an oxide is substituted by another element, not an anhydride. Thus in $\left.\begin{matrix}O\\O\end{matrix}\right\}$ Hg we find part of the O gone in the oxychloride, $\left.\begin{matrix}O\\Cl\end{matrix}\right\}$ Hg; and in various sesquioxides, as sesquioxide of uranium and chromium, we find analogous compounds, $\overset{\text{Sesquioxide uranium.}}{\left.\begin{matrix}O_2\\O\end{matrix}\right\} Ur_2}$, like $\overset{\text{Chloride of uranyl.}}{\left.\begin{matrix}O_2\\Cl\end{matrix}\right\} Ur_2}$; and also in Peligot's oxychloride of chromium, $\overset{\text{Sesquioxide chromium.}}{\left.\begin{matrix}O_2\\O\end{matrix}\right\} Cr_2}$, like $\overset{\text{Chloride of chromium.}}{\left.\begin{matrix}O_2\\Cl\end{matrix}\right\} Cr_2}$.

We also find that in glycol ether, where ethylene plays the part of a metal, that the two atoms of oxygen can be replaced by an anhydride.

Glycol ether - - - -	$C_4\,H_4\,O_2$
Isethionic anhydride - - -	$C_4\,H_4\,(S\,O_3)_2$

It is not required by the theory that such complete substitutions for oxygen should occur, as shown in the case of Isethionic acid (although they do occur in organo-metallic bodies), because the lower oxides act as moveable radicals, and should not be displaced. We have written a peroxide as M $\left\{\begin{matrix}O\\O\end{matrix}\right.$ to contrast it with $\left.\begin{matrix}H\\H\end{matrix}\right\}$ O_2; but in reality it is viewed as MO, O, in which M O acts as a compound radical, and we should no more expect to substitute the oxygen of the protoxide, than the hydrogen of ethyl.

1138. Hitherto we have confined ourselves, for simplicity, to Dr. Playfair's views of the constitution of neutral salts; but he does not attempt to fit all salts into the one type, HO_2, as the supporters of the water type fit all salts into the one type, H_2O_2, or its multiples. On the contrary, he takes as types all the oxides which commonly occur. These are,—

	Formulæ.	Formulæ as containing previous oxides.	Salt types.	
Suboxides	M_2O			
Protoxides	M_2O_2	$= M_2O, O$	like M_2O, A	salts of suboxides.
Magnetic oxides	M_3O_4	$= M_3O_3, O$	,, M_3O_3, A	tribasic salts & subsalts.
Sesquioxides	M_2O_3	$= M_2O_2, O$	,, M_2O_2, A	bibasic salts & subsalts.
PEROXIDES	M_2O_4	$= M_2O_2, O_2$	,, M_2O_2, A_2	neutral salts.
Acid Oxides	M_2O_6	$= M_2O_3, O_3$	,, M_2O_3, A_3	salts of sesquioxides.

In the above formulæ the oxides are written first with their arbitrary formulæ; then rationally, as being higher oxides of previous lower oxides, acting as radicals; and in the last column the letter A signifies any acid which may substitute this replaceable oxygen. According to these views, the only truly neutral salts are represented by the only neutral oxide, the peroxide of a metal; but the more rarely occurring salts, such as tribasic or bibasic phosphates, appear upon the type of oxides having still fully basic characters, while the characteristic acid salts of the sesquioxides are constituted on the type of manganic acid.

1139. Dr. Playfair extends these views to organic compounds, and shows that they equally apply to them. We will formulate, in accordance with his views, a few of the ethers and alcohols as examples:—

(1.) Each lower oxide endeavours to unite either with an equivalent of oxygen, of water, or of acid, as the case may be, to gratify its atomicity. When the addition is only one equivalent, we have compounds like the monatomic alcohols; thus, $MO + O = MO_2$.

Potash, K_2O_2; hydrate, KO, HO; salt, KO, NO_5.
Ether, $(C_4H_5O)_2$; alcohol, C_4H_5O, HO; compound ethers, C_4H_5O, NO_5.

(2.) But when a sesquioxide is the starting-point, this oxide, being monatomic, forms alcohols and salts after its own fashion, $M_2O_3 + O_3 = M_2O_6$.

Sesquioxide of iron, Fe_2O_3; its hydrate, $Fe_2O_3\,3\,HO$;
its salts, $Fe_2O_3\,3\,A$.
Glycerin ether, C_6H_5,O_3; glycerin, $C_6H_5O_3, 3\,HO$;
glycerides, $C_6H_5O_3, 3\,A$.

(3.) And when a biatomic oxide is the starting-point, we have the new and important class of biatomic alcohols:—

Peroxide of tin, Sn_2O_2; its hydrate, $Sn_2O_2, 2\,HO$;
and its salt, $Sn_2O_2, 2\,A$.
Ethylene ether, $C_4H_4O_2$; glycol, $C_4H_4O_2, 2\,HO$;
and its salts, $C_4H_4O_2, 2\,A$.

(4.) According to Dr. Playfair's views, in which a radical is considered as the moveable part of a compound in a given set of reactions, there may be primary and secondary radicals in the same compound. Thus in peroxide of lead, the metal is the primary radical, and the protoxide a secondary radical, PbO, O. Applying this to the alcohols, chemical organic compounds can be classified in a simple way. Under one set of reactions, the alcohols yield the alcohol radicals, such as ethyl; under another set they yield the olifenes, as ethylene. An olifene may be thus a hydrocarbon, or have part of its hydrogen substituted by oxygen, thus:—

Ethylene - - - - -	(C_4H_4)
Oxidized radical - - - -	$(C_4H_2O_2)$

In both cases they are biatomic, and their compounds are the results of this completed biatomicity. If only one of the two atoms be filled up, we have radicals, as—

Ethyl - - - - - -	(C_4H_4H)
Acetyl - - - - -	$(C_4H_2O_2, H)$

When both the atoms are filled up, we have neutral compounds, as—

Hydride of ethyl - - -	$(C_4H_4)\,H, H$
Aldehyde - - - -	$(C_4H_2O_2)\,H, H$

The compounds of these olifenes now run in a series perfectly parallel, and of a remarkably simple relation:—

Hydride of ethyl, $(C_4H_4)\,H,H$; aldehyde, $(C_4H_2O_2)\,H, H$.
Ether, $(C_4H_4)\,H, O$; acetic anhydride, $(C_4H_2O_2)\,H, O$.

Alcohol, $(C_4H_4)H, O + HO$; acetic acid, $(C_4H\ O_2)H, O + HO$.

Glycol ether, $(C_4H_4)O, O$; glycolid, $(C_4H_2O_4)O, O$.

Glycol, $(C_4H_4)O, O + 2HO$; glycolic acid, $(C_4H_2O_2)O, O + 2HO$.

In these formulæ it will be seen that the aldehydes correspond to the marsh gas compounds of the alcohols, while the anhydrides correspond to the ethers, and the acids to the alcohols; the biatomic alcohols and acids belonging to the same, and not to a different system.

1140. *Dr. Frankland's views.*—A general outline of Dr. Frankland's views may be expressed in a few words. He considers that the elements are capable of uniting with *only a certain number of atoms* of other elements, or of compound radicals playing the parts of elementary bodies; and this number of atoms with which the elements are capable of uniting is definite and unalterable, no matter what the character of the uniting atoms may be. "When the formulæ of inorganic chemical compounds are considered, even a superficial observer is struck with the general symmetry of their construction. The compounds of nitrogen, phosphorus, antimony, and arsenic especially, exhibit the tendency of these elements to form compounds containing three or five equivalents of other elements; and it is in these proportions that their affinities are best satisfied. Thus in the trinal group we have NO_3, NH_3, NI_3, NS_3, PO_3, PH_3, PCl_3, SbO_3, SbH_3, $SbCl_3$, AsO_3, AsH_3, $AsCl_3$, &c.; and in the five-atom group, NO_5, NH_4O, NH_4I, PO_5, PH_4I, &c." Frankland considers that the organo-metallic bodies are constructed upon the types of the inorganic chlorides, sulphides, oxides, &c., of the respective metals which they contain; the chlorine, oxygen, sulphur, &c., being replaced in equivalent proportion, and step by step, by the alcohol radicals. It will thus be seen that the views of Dr. Playfair and Dr. Frankland are much in accord as to the manner in which bodies are constructed.

1141. It is necessary, in order fully to understand Frankland's views, to be well acquainted with the chemical composition and properties of the principal organo-metallic bodies; we will therefore describe the composition and properties of these bodies* more fully than we have hitherto done, before entering more into detail with regard to Frankland's views. We will commence with a description of the organo-potassium, sodium, magnesium, zinc, and cadmium compounds. These organo-metallic bodies are all formed, according to Frankland, upon the models of the protochlorides of these metals, the general type being,—

$$M_2 \left\{ \begin{matrix} Cl \\ Cl \end{matrix} \right.$$

Only one member of the cadmium series is known, and that very imperfectly. The potassium and sodium series are known only in combination with the corresponding zinc compounds. Example:—$2\,Zn_2 \left\{ \begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix} \right. + Na_2 \left\{ \begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix} \right.$.

1142. Three bodies belonging to the zinc series are known, viz.:—

Zinc-methyl - - - - - -	$Zn_2 \left\{ \begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix} \right.$
Zinc-ethyl - - - - - -	$Zn_2 \left\{ \begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix} \right.$
Zinc-amyl - - - - - -	$Zn_2 \left\{ \begin{matrix} C_{10}H_{11} \\ C_{10}H_{11} \end{matrix} \right.$

These bodies are colourless, transparent, mobile, volatile, and odorous liquids, composed of four gaseous volumes of the hydrocarbon radical, and two volumes of zinc vapour, the six volumes condensed to four. The methyl and ethyl compounds are spontaneously inflammable, burning with a greenish-blue flame. In contact with water they are instantly decomposed, with formation of oxide of zinc and hydride of the organic radical.

1143. Of the magnesium series, the compounds containing ethyl and methyl only have hitherto been examined, and the former alone submitted to analysis. These bodies possess a close similarity to organo-zinc compounds. They are very volatile colourless liquids, possessing a powerful alliaceous odour, are spontaneously inflammable, and decompose water with violence.

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* I have taken the description of these bodies from Frankland's paper on the organo-metals. I have merely altered the arrangement and condensed the report. I have given, in Appendix M, the general methods for forming these bodies, which I have taken from the same source.

1144. The organo-aluminum and glucinum compounds are formed upon the type of the sesquichloride of those metals,—

$$M_2\left\{\begin{array}{l}Cl\\Cl\\Cl\end{array}\right.$$

These organo-compounds have not been isolated with certainty; they are known only in combination with the iodides of the respective metals. These double compounds possess great chemical energy; they are spontaneously inflammable, volatile liquids, which decompose water with explosive violence. They are attacked by zinc-ethyl, forming iodide of zinc, and very inflammable liquids, which latter are believed to be the pure organo-compounds.

1145. The organo-tin compounds are represented by the three chlorides of tin,—

$$Sn_2\left\{\begin{array}{l}Cl\\Cl\end{array}\right. \qquad Sn_2\left\{\begin{array}{l}Cl\\Cl\\Cl\end{array}\right. \qquad Sn_2\left\{\begin{array}{l}Cl\\Cl\\Cl\\Cl\end{array}\right.$$

A large number of organo-metallic bodies containing tin has been described. The existence of the following may be considered as clearly established:—

(*a.*) *Stannous compounds.*

Stannous methide, or stanmethyl - $Sn_2\left\{\begin{array}{l}C_2H_3\\C_2H_3\end{array}\right.$

Stannous ethide, or stanethyl - - $Sn_2\left\{\begin{array}{l}C_4H_5\\C_4H_5\end{array}\right.$

These compounds are oily liquids, soluble in alcohol and ether, but insoluble in water, and possessing a pungent odour. They cannot be distilled without decomposition, being resolved into stannic compounds and metallic tin.

(*b.*) *Sesqui-compounds.*

Sesquimethide of tin - - $Sn_2\left\{\begin{array}{l}C_2H_3\\C_2H_3\\C_2H_3\end{array}\right.$

Dimethiodide of tin - - $Sn_2\left\{\begin{array}{l}C_2H_3\\C_2H_3\\I\end{array}\right.$

Sesquiethide of tin - - $Sn_2\left\{\begin{array}{l}C_4H_5\\C_4H_5\\C_4H_5\end{array}\right.$ Diethiodide of tin - $Sn_2\left\{\begin{array}{l}C_4H_5\\C_4H_5\\I\end{array}\right.$

The sesqui-compounds of the form $Sn_2\left\{\begin{array}{l}R+\\R+\\R+\end{array}\right.$ have hitherto been very little examined. They are oily liquids, and are capable of uniting directly with negative radicals.

The sesqui-compounds of the form $Sn_2\left\{\begin{array}{l}R+\\R+\\R-\end{array}\right.$ are very little known; diethiodide of tin, above mentioned, being the only one known with certainty.

(*c.*) *Stannic compounds.*

Stannic methide $Sn_2\left\{\begin{array}{l}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\end{array}\right.$ Stannic ethylotrimethide - $Sn_2\left\{\begin{array}{l}C_2H_3\\C_2H_3\\C_2H_3\\C_4H_5\end{array}\right.$

Stannic ethide - $Sn_2\left\{\begin{array}{l}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{array}\right.$ Stannic iodotrimethide - $Sn_2\left\{\begin{array}{l}C_2H_3\\C_2H_3\\C_2H_3\\I\end{array}\right.$

Stannic ethylomethide - $Sn_2\left\{\begin{array}{l}C_2H_3\\C_2H_3\\C_4H_5\\C_4H_5\end{array}\right.$ Stannic iodotriethide - $Sn_2\left\{\begin{array}{l}C_4H_5\\C_4H_5\\C_4H_5\\I\end{array}\right.$

Stannic iododimethide - $Sn_2\left\{\begin{array}{l}C_2H_3\\C_2H_3\\I\\I\end{array}\right.$ Stannic iododiethide - $Sn_2\left\{\begin{array}{l}C_4H_5\\C_4H_5\\I\\I\end{array}\right.$

Stannic compounds of the form $Sn_2\left\{\begin{array}{l}R+\\R+\\R+\\R+\end{array}\right.$ are colourless mobile liquids, possessing a slight etherial odour. They are volatile without decomposition, and are very stable.

Stannic compounds of the form $Sn_2\left\{\begin{array}{l}R+\\R+\\R+\\R-\end{array}\right.$ commonly called compounds of sesquistanethyl, have been comparatively well studied. The oxides are, in the anhydrous condition, volatile, limpid, oily liquids, which readily unite with water, forming crystalline hydrates, which have a powerful alkaline reaction, and neutralize the strongest acids, forming an extensive series of salts. These salts are almost all soluble in water, readily crystallizable, and of a very pungent odour. The iodostannic triethide has the following formula,—

$$Sn_2\left\{\begin{array}{l}C_4H_5\\C_4H_5\\C_4H_5\\\quad I\end{array}\right.$$

Stannic compounds of the form $Sn_2\left\{\begin{array}{l}R+\\R+\\R-\\R-\end{array}\right.$ have also been very completely investigated. The oxides are white amorphous powders, insoluble in water, alcohol, and ether. They dissolve in hydrochloric, hydriodic, and hydrobromic acids, forming colourless and inodorous salts, which crystallize in fine prisms. Most of the oxysalts can also be obtained in the crystalline form, either from aqueous or alcoholic solutions. Iodide of stannic diethide, which may be regarded as the representative of the haloid salts, has the following formula,—$Sn_2\left\{\begin{array}{l}C_4H_5\\C_4H_5\\\quad I\\\quad I\end{array}\right.$

1146. The compounds of the bismuth series are represented by the terchloride of bismuth and by bismuthic acid :—

$$Bi\left\{\begin{array}{l}Cl\\Cl\\Cl\end{array}\right. \qquad Bi\left\{\begin{array}{l}O\\O\\O\\O\\O\end{array}\right.$$

The following bodies belonging to this series have been described:—

Bismuthous triethide - -	$Bi\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.$	Bismuthous di-iodoethide - .	$Bi\left\{\begin{matrix}C_4H_5\\I\\I\end{matrix}\right.$
Bismuthous dichlorethide -	$Bi\left\{\begin{matrix}C_4H_5\\Cl\\Cl\end{matrix}\right.$	Bismuthous dioxyethide -	$Bi\left\{\begin{matrix}C_4H_5\\O\\O\end{matrix}\right.$

Double compound of bismuthous sulphide with bismuthic sulphotriethide - - - $Bi\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\S\\S\end{matrix}\right. + 2\,Bi\left\{\begin{matrix}S\\S\\S\end{matrix}\right. ?$

These bodies have as yet been but very imperfectly investigated. The triethide compound is a colourless, or slightly yellow, mobile liquid, having an unpleasant odour, like that of stibethine. Exposed to the air, it gives off dense yellow fumes, inflames spontaneously, and finally explodes. It is very instable; it begins to decompose at 50° or 60° C., and explodes violently when heated to 150° C., a temperature still below its boiling point.

1147. The organo-lead compounds are moulded on the types of sesquioxide and peroxide of lead:—

$$Pb_2\left\{\begin{matrix}O\\O\\O\end{matrix}\right. \qquad Pb_2\left\{\begin{matrix}O\\O\\O\\O\end{matrix}\right.$$

The following are at present the only known bodies belonging to this series, the ethyl group alone having been explored:—

Sesqui-plumbethide -	$Pb_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right. ?$	Plumbic chlorotriethide -	$Pb_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\Cl\end{matrix}\right.$
Plumbic oxytriethide - -	$Pb_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\O\end{matrix}\right.$	Plumbic triethylonitrate	$Pb_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\NO_6\end{matrix}\right.$

Plumbic ethide - - - - - $Pb_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.$

The existence of the first of these bodies has not yet been clearly established. Plumbic ethide is a colourless, limpid fluid, soluble in ether, but insoluble in water, and possessing a faint odour.

1148. The mercuric series are all moulded upon the type of the bichloride,—

$$Hg\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$$

No organo-mercurous compounds have yet been produced; the mercuric series comprise the following members:—

Mercuric methiodide -	$Hg\left\{\begin{matrix}C_2H_3\\I\end{matrix}\right.$	Mercuric ethiodide -	$Hg\left\{\begin{matrix}C_4H_5\\I\end{matrix}\right.$
Mercuric meth-hydrate	$Hg\left\{\begin{matrix}C_2H_3\\H\,O_2\end{matrix}\right.$	Mercuric ethohydrate -	$Hg\left\{\begin{matrix}C_4H_5\\H\,O_2\end{matrix}\right.$
Mercuric methonitrate -	$Hg\left\{\begin{matrix}C_2H_3\\N\,O_6\end{matrix}\right.$	Mercuric ethonitrate -	$Hg\left\{\begin{matrix}C_4H_5\\N\,O_6\end{matrix}\right.$
Mercuric methide -	$Hg\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.$	Mercuric ethide	$Hg\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.$

Mercuric ethylomethide - - $Hg\left\{\begin{matrix}C_4H_5\\C_2H_3\end{matrix}\right.?$

Mercuric methide and mercuric ethide are colourless, etherial, volatile liquids, insoluble in water, but soluble in alcohol and ether, and possessing great stability. Mercuric methide possesses the highest specific gravity of any known non-metallic liquid (3·069). Glass, consequently, floats upon its surface. The hydrates of mercuric methoxide and mercuric ethoxide are caustic alkaline bases, capable of expelling ammonia from its salts. The remaining mercury compounds, which may be considered as derivatives of these two bodies, are represented in the list by the iodides and nitrates; they generally crystallize very readily, and, with the exception of the haloid compounds, are soluble in water. When their aqueous solutions are treated with zinc, they are decomposed, the zinc becomes amalgamated, and gaseous hydrides of the positive radicals are evolved.

1149. The arsenic and antimony series have for their types the following inorganic compounds:—

$$\mathrm{As}\left\{\begin{matrix}\mathrm{S}\\\mathrm{S}\end{matrix}\right. \qquad \mathrm{As}\left\{\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right. \qquad \mathrm{As}\left\{\begin{matrix}\mathrm{O}\\\mathrm{O}\\\mathrm{O}\\\mathrm{O}\\\mathrm{O}\end{matrix}\right. \qquad \mathrm{Sb}\left\{\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right. \qquad \mathrm{Sb}\left\{\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right.$$

1150. The antimony series of organo-metallic bodies contains a greater number and variety of compounds than any other, with the exception of the arsenic series. The remarkable polyatomic character of antimony and arsenic not only renders the possible number of their organo-compounds very large, but the variation in the proportions of the positive and negative molecules gives an extremely wide range to their chemical character, extending as it does, from highly caustic bases on the one hand, to powerful bibasic acids on the other. The following are the principal compounds belonging to this series:—

Trimethyl-stibine - - - -	$\mathrm{Sb}\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right.$
Antimonic trimethoxide - - -	$\mathrm{Sb}\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\\mathrm{O}\\\mathrm{O}\end{matrix}\right.$
Antimonic trimethochloride - -	$\mathrm{Sb}\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right.$
Iodide of tetramethyl-stibonium, or antimonic tetramethiodide - -	$\mathrm{Sb}\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\\\mathrm{I}\end{matrix}\right.$

Hydrate of tetramethyl-stibonium, or antimonic tetramethyl-hydrate	$Sb\left\{\begin{array}{l}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\\HO_2\end{array}\right.$
Antimonic trimethonitrate	$Sb\left\{\begin{array}{l}C_2H_3\\C_2H_3\\C_2H_3\\NO_6\\NO_6\end{array}\right.$
Triethyl-stibine	$Sb\left\{\begin{array}{l}C_4H_5\\C_4H_5\\C_4H_5\end{array}\right.$
Antimonic triethoxide	$Sb\left\{\begin{array}{c}C_4H_5\\C_4H_5\\C_4H_5\\O\\O\end{array}\right.$
Antimonic triethochloride	$Sb\left\{\begin{array}{c}C_4H_5\\C_4H_5\\C_4H_5\\Cl\\Cl\end{array}\right.$
Iodide of tetrethyl-stibonium, or antimonic tetramethiodide	$Sb\left\{\begin{array}{c}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\\I\end{array}\right.$
Iodide of methylo-triethyl-stibonium, or antimonic triethomethiodide	$Sb\left\{\begin{array}{c}C_4H_5\\C_4H_5\\C_4H_5\\C_2H_3\\I\end{array}\right.$
Hydrate of tetrethyl-stibonium, or antimonic tetrethyl-hydrate	$Sb\left\{\begin{array}{l}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\\HO_2\end{array}\right.$

Antimonic triethonitrate	$Sb\left\{\begin{array}{l} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ NO_6 \\ NO_6 \end{array}\right.$
Nitrate of tetrethyl-stibonium, or antimonic tetrethyl-nitrate	$Sb\left\{\begin{array}{l} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ NO_6 \end{array}\right.$
Antimonic triethantimonite	$Sb\left\{\begin{array}{l} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ SbO_4 \\ SbO_4 \end{array}\right.$
Antimonic triethoxiodide	$Sb\left\{\begin{array}{c} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ O \\ I \end{array}\right.$
Triamyl-stibine	$Sb\left\{\begin{array}{l} C_{10}H_{11} \\ C_{10}H_{11} \\ C_{10}H_{11} \end{array}\right.$
Antimonic triamyl-chloride	$Sb\left\{\begin{array}{c} C_{10}H_{11} \\ C_{10}H_{11} \\ C_{10}H_{11} \\ Cl \\ Cl \end{array}\right.$
Antimonic triamyl-nitrate	$Sb\left\{\begin{array}{l} C_{10}H_{11} \\ C_{10}H_{11} \\ C_{10}H_{11} \\ NO_6 \\ NO_6 \end{array}\right.$

It is remarkable that we have as yet no decisive evidence in the antimony series of the existence of a compound corresponding to cacodyl. It is true that such a body has been described under the name of *stibbiamyl*, but subsequent experiments have failed to confirm its existence. Amongst organo-antimony compounds, therefore, the most simple form is $\mathrm{Sb}\left\{\begin{matrix}R+\\R+\\R+\end{matrix}\right.$. Bodies of this form are the analogues of ammonia, and have been already described under that type. The bodies also having the form $\mathrm{Sb}\left\{\begin{matrix}R+\\R+\\R+\\R+\\R-\end{matrix}\right.$ have been described. We shall therefore only notice here the bodies having the form $\mathrm{Sb}\left\{\begin{matrix}R+\\R+\\R+\\R-\\R-\end{matrix}\right.$ and their derivatives. When the two atoms of R— are oxygen, these compounds constitute what may be termed biacid antimony bases. They are formed either by the direct union of the stibamines $\left(\mathrm{Sb}\left\{\begin{matrix}R+\\R+\\R+\end{matrix}\right.\right)$ with oxygen, $\mathrm{Sb}\left\{\begin{matrix}R+\\R+\\R+\end{matrix}\right. + O_2 = \mathrm{Sb}\left\{\begin{matrix}R+\\R+\\R+\\O\\O\end{matrix}\right.$, or by the decomposition of the corresponding haloid compounds by means of potash, thus:—

$$\mathrm{Sb}\left\{\begin{matrix}R+\\R+\\R+\\Cl\\Cl\end{matrix}\right. + 2\,KO = \mathrm{Sb}\left\{\begin{matrix}R+\\R+\\R+\\O\\O\end{matrix}\right. + 2\,KCl$$

The stibamines, although in other respects the perfect analogues of the nitramines, here evidently exhibit a much more highly positive character, uniting with oxygen so energetically as to be spontaneously inflammable in the lower portion of the series.

The biacid antimony bases are colourless, transparent, amorphous, and tenacious bodies. The ethyl base is easily soluble in water and alcohol, but somewhat less soluble in ether. These bases possess a bitter taste, are non-volatile, and do not suffer any change when exposed to the air. Treated with potassium, they are reduced to stibamines,—

$$Sb\begin{cases}R+\\R+\\R+\\O\\O\end{cases}+2K=Sb\begin{cases}R+\\R+\\R+\end{cases}+2KO$$

Fuming nitric acid decomposes the biacid bases with ignition; but when they are treated with dilute nitric or other acid, the respective biacid salts are produced. The oxy-salts are soluble in water or alcohol. Most of them crystallize without much difficulty, as do also the antimonic biniodides; but antimonic trietho-bromide, and trietho-chloride are liquids not volatile without decomposition, insoluble in water, but soluble in alcohol and ether.

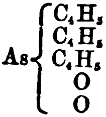
1151. The arsenic series is perhaps the most important and interesting amongst organo-metallic bodies. It contains the first-discovered organo-metal, cacodyl, the classical investigation of which, by Bunsen, not only imparts a completeness to our knowledge of this series, but has afforded the clue to the successful interpretation of many phenomena met with in other analogous families. The following are the principal organo-arsenical compounds already investigated:—

Cacodyl - - - - -	$As\begin{cases}C_2H_3\\C_2H_3\end{cases}$
Ethylic cacodyl - - - -	$As\begin{cases}C_4H_5\\C_4H_5\end{cases}$
Butylic cacodyl - - - -	$As\begin{cases}C_8H_9\\C_8H_9\end{cases}$
Oxide of cacodyl - - -	$As\begin{cases}C_2H_3\\C_2H_3\\O\end{cases}$
Sulphide of cacodyl - - -	$As\begin{cases}C_2H_3\\C_2H_3\\S\end{cases}$

Chloride of cacodyl - - -	$\mathrm{As}\left\{\begin{array}{l}C_2H_3\\ C_2H_3\\ \;\;Cl\end{array}\right.$
Chloride of cacoplatyl - -	$\mathrm{As}\left\{\begin{array}{l}C_2H_3\\ C_2Pt'H\\ \;\;Cl\end{array}\right.$
Arsenious dioxymethide - -	$\mathrm{As}\left\{\begin{array}{l}C_2H_3\\ \;\;O\\ \;\;O\end{array}\right.$
Arsenious disulphomethide -	$\mathrm{As}\left\{\begin{array}{l}C_2H_3\\ \;\;S\\ \;\;S\end{array}\right.$
Arsenious dichloromethide -	$\mathrm{As}\left\{\begin{array}{l}C_2H_3\\ \;\;Cl\\ \;\;Cl\end{array}\right.$
Trimethylarsine - - -	$\mathrm{As}\left\{\begin{array}{l}C_2H_3\\ C_2H_3\\ C_2H_3\end{array}\right.$
Arsenious diethiodide - -	$\mathrm{As}\left\{\begin{array}{l}C_4H_5\\ C_4H_5\\ \;\;I\end{array}\right.$
Triethylarsine - - - -	$\mathrm{As}\left\{\begin{array}{l}C_4H_5\\ C_4H_5\\ C_4H_5\end{array}\right.$
Monomethylarsenic acid - -	$\mathrm{As}\left\{\begin{array}{l}C_2H_3\\ \;\;O\\ \;\;O\\ \;\;O\\ \;\;O\end{array}\right.$
Monomethylarseniates - -	$\mathrm{As}\left\{\begin{array}{l}C_2H_3\\ \;\;O\\ \;\;O\\ MO_2\\ MO_2\end{array}\right.$
Arsenic dioxydichlormethide -	$\mathrm{As}\left\{\begin{array}{l}C_2H_3\\ \;\;O\\ \;\;O\\ \;\;Cl\\ \;\;Cl\end{array}\right.$

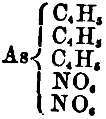
Arsenic tetrachlormethide - -	$As\left\{\begin{matrix}C_2H_3\\Cl\\Cl\\Cl\\Cl\end{matrix}\right.$
Cacodylic acid - - - -	$As\left\{\begin{matrix}C_2H_3\\C_2H_3\\O\\O\\O\end{matrix}\right.$
Cacodylates - - - -	$As\left\{\begin{matrix}C_2H_3\\C_2H_3\\O\\O\\MO_2\end{matrix}\right.$
Sulphocacodylic acid - - -	$As\left\{\begin{matrix}C_2H_3\\C_2H_3\\S\\S\\S\end{matrix}\right.$
Sulphocacodylates - - -	$As\left\{\begin{matrix}C_2H_3\\C_2H_3\\S\\S\\MS_2\end{matrix}\right.$
Terchloride of cacodyl - -	$As\left\{\begin{matrix}C_2H_3\\C_2H_3\\Cl\\Cl\\Cl\end{matrix}\right.$
Ethyl-cacodylic acid - - -	$As\left\{\begin{matrix}C_4H_5\\C_4H_5\\O\\O\\O\end{matrix}\right.$
Ethyl-cacodylates - - -	$As\left\{\begin{matrix}C_4H_5\\C_4H_5\\O\\O\\MO_2\end{matrix}\right.$

Arsenic triethoxide - - -



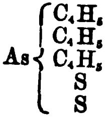
$$As\left\{\begin{array}{c}C_4H_5\\C_4H_5\\C_4H_5\\O\\O\end{array}\right.$$

Arsenic triethonitrate - - -



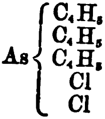
$$As\left\{\begin{array}{c}C_4H_5\\C_4H_5\\C_4H_5\\NO_6\\NO_6\end{array}\right.$$

Arsenic triethosulphide - -



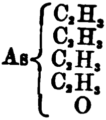
$$As\left\{\begin{array}{c}C_4H_5\\C_4H_5\\C_4H_5\\S\\S\end{array}\right.$$

Arsenic triethochloride - -



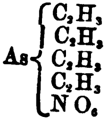
$$As\left\{\begin{array}{c}C_4H_5\\C_4H_5\\C_4H_5\\Cl\\Cl\end{array}\right.$$

Oxide of tetramethylarsonium, or arsenic tetramethoxide - -



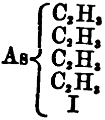
$$As\left\{\begin{array}{c}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\\O\end{array}\right.$$

Nitrate of tetramethylarsonium, or arsenic tetramethyl-sulphate



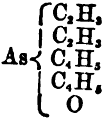
$$As\left\{\begin{array}{c}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\\NO_6\end{array}\right.$$

Iodide of tetramethylarsonium, or arsenic tetramethiodide -



$$As\left\{\begin{array}{c}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\\I\end{array}\right.$$

Oxide of dimethyl-diethylarsonium, or arsenic dimethyldiethyloxide - - - -



$$As\left\{\begin{array}{c}C_2H_3\\C_2H_3\\C_4H_5\\C_4H_5\\O\end{array}\right.$$

Iodide of dimethyl-diethylarsonium, or arsenic dimethyl-diethyliodide - - - -	$As\begin{cases} C_2H_3 \\ C_2H_3 \\ C_4H_5 \\ C_4H_5 \\ I \end{cases}$
Nitrate of dimethyl-diethylarsonium, or arsenic dimethyl-diethyl-nitrate - - - -	$As\begin{cases} C_2H_3 \\ C_2H_3 \\ C_4H_5 \\ C_4H_5 \\ NO_6 \end{cases}$
Oxide of tetrethylarsonium, or arsenic tetrethoxide - - -	$As\begin{cases} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ O \end{cases}$
Nitrate of tetrethylarsonium, or arsenic tetrethyl-nitrate - -	$As\begin{cases} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ NO_6 \end{cases}$
Chloride of tetrethylarsonium, or arsenic tetrethyl-chloride - -	$As\begin{cases} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ Cl \end{cases}$
Iodide of dimethyl-diamylarsonium, or arsenic dimethamyliodide	$As\begin{cases} C_2H_3 \\ C_2H_3 \\ C_{10}H_{11} \\ C_{10}H_{11} \\ I \end{cases}$

The organo-arsenical compounds belonging to the type $As\begin{cases} R \\ R \end{cases}$ contain only positive radicals. They are volatile poisonous liquids, insoluble in water, but very soluble in alcohol and ether, and possessing an insupportable odour. The lower members of the family are spontaneously inflammable, whilst the higher ones also rapidly oxidize in air. They unite with negative elements with great energy, manifesting in their combinations either a uniatomic or a teratomic character, and producing bodies either of the form $\text{As}\left\{\begin{matrix}R+\\R+\\R-\end{matrix}\right.$ or $\text{As}\left\{\begin{matrix}R+\\R+\\R-\\R-\\R-\end{matrix}\right.$ Thus, cacodyl forms with chlorine, chloride of cacodyl and terchloride of cacodyl.

Methyl-cacodyl boils at 170° C., and ethylic cacodyl between 185° and 190° C. Heated to 400° C., cacodyl splits up into metallic arsenic, hydride of methyl, and olefiant gas. Bodies of the cacodyl type can be re-generated by reducing agents from many of their uniatomic compounds: thus, chloride of cacodyl and metallic zinc give cacodyl and chloride of zinc.

The bodies constructed on the type $\text{As}\left\{\begin{matrix}R\\R\\R\end{matrix}\right.$ are of three forms, viz.:—(1) $\text{As}\left\{\begin{matrix}R+\\R+\\R+\end{matrix}\right.$ (2) $\text{As}\left\{\begin{matrix}R+\\R+\\R-\end{matrix}\right.$ (3) $\text{As}\left\{\begin{matrix}R+\\R-\\R-\end{matrix}\right.$ Those belonging to the first are termed arsines, and have been described under the ammonia type; but, in addition to the alkaloid function, they have, like the corresponding antimony compounds, the power of combining with two negative atoms, forming bodies of the type $\text{As}\left\{\begin{matrix}R+\\R+\\R+\\R-\\R-\end{matrix}\right.$ Thus, triethylarsine combines with oxygen to form arsenic dioxytriethide. The lower members of the type possess this property to such an extent as to render them spontaneously inflammable in air.

Compounds belonging to the second of the above forms are produced by the direct combination of the cacodyls with negative elements; the oxides are bases of comparatively feeble power, slowly combining with two additional equivalents of oxygen to form acids. Thus, oxide of cacodyl, by exposure to air, slowly passes into cacodylic acid. The chlorine, bromine, and iodine compounds of this second form are volatile neutral bodies, which may be regarded as the haloid salts of cacodyl. Heated in contact with bichloride of platinum, the chloride of cacodyl presents an interesting reaction; two equivalents of hydrogen in the cacodyl become replaced by a biatomic molecule of platinum, producing chloride of cacoplatyl, thus:—

$$As\left\{\begin{array}{l}C_2H_3\\C_2H_3\\\quad Cl\end{array}\right. + Pt\,Cl_2 = As\left\{\begin{array}{l}C_2H_3\\C_2Pt''H\\\quad Cl\end{array}\right. + H\,Cl$$

Cacoplatyl forms a series of compounds analogous to those of cacodyl.

The only compounds of the third form yet known belong to the methylic group. Arsenious dioxymethide is a crystalline body of a neutral character, soluble in water, alcohol, and ether, unchanged by exposure to air, but transformed by distillation with hydrate of potash into arsenious acid and oxide of cacodyl. Hydrochloric acid converts it into arsenious dichlormethide, and hydrobromic and hydriodic acids produce a perfectly analogous change; whilst sulphuretted hydrogen transforms it into arsenious disulphomethide. The chlorine, bromine, and iodine compounds are neutral bodies of considerable stability; the two former are liquid, the latter solid and crystalline. By the action of chlorine, or oxidizing agents, they are transformed into bodies of the form $As\left\{\begin{array}{l}R+\\R-\\R-\\R-\\R-\end{array}\right.$

1152. The bodies constructed on the type $As\left\{\begin{array}{l}R\\R\\R\\R\\R\end{array}\right.$ have been more thoroughly investigated than those of any other type; those constructed on the type $As\left\{\begin{array}{l}R+\\R+\\R+\\R+\\R-\end{array}\right.$ are the strict analogues of the compounds of ammonium, and have been described under that type. Bodies on the type

$\mathrm{As}\left\{\begin{matrix}\mathrm{R}+\\ \mathrm{R}-\\ \mathrm{R}-\\ \mathrm{R}-\\ \mathrm{R}-\end{matrix}\right.$ have only yet been explored in the methylic group. The oxygen compound constitutes anhydrous monomethylarsenic acid,—a direct derivative from arsenious dioxymethide:—

Arsenious dioxymethide.	Monomethylarsenic acid.

$$\mathrm{As}\left\{\begin{matrix}C_2H_3\\ O\\ O\end{matrix}\right. + 2\,\mathrm{Ag\,O} = \mathrm{As}\left\{\begin{matrix}C_2H_3\\ O\\ O\\ O\\ O\end{matrix}\right. + 2\,\mathrm{Ag}$$

Monomethylarsenic acid is bibasic, forming stable and well-defined crystallizable salts, the formulæ of which are represented by the general expression,—

$$\mathrm{As}\left\{\begin{matrix}C_2H_3\\ O\\ O\\ M\,O_2\\ M\,O_2\end{matrix}\right.$$

The chlorine compound is exceedingly unstable; it may, however, be formed at —10° C., but is transformed at 0° C. into arsenious chloride and chloride of methyl. Arsenic dioxydichlor-methide is a somewhat more stable body, formed by the direct union of chlorine with arsenious dioxymethide. Nevertheless, even this compound readily decomposes, with evolution of chloride of methyl.

1153. The oxygen compounds on the type $\mathrm{As}\left\{\begin{matrix}\mathrm{R}+\\ \mathrm{R}+\\ \mathrm{R}-\\ \mathrm{R}-\\ \mathrm{R}-\end{matrix}\right.$ are feeble monobasic acids, of which cacodylic acid may be regarded as the representative. They are derived from the bodies $\mathrm{As}\left\{\begin{matrix}\mathrm{R}+\\ \mathrm{R}+\\ \mathrm{O}\end{matrix}\right.$ by direct oxidation. Cacodylic acid is remarkable for its stability; neither fuming nitric acid nor a mixture of sulphuric and chromic acids attacks it, even at the boiling point, and it may be heated to 200° C. without alteration. Although it is soluble in water, and contains upwards of 54 per cent. of arsenic, yet it is not in the least degree poisonous. Several agents reduce cacodylic acid to the arsenious, or even to the diatomic form. Thus, phosphorous acid transforms it into cacodyl; zinc also produces the same result. Hydriodic acid gas converts it into arsenious dimethiodide. Its acid character is so slightly marked that it is capable of forming compounds in which it appears to play the part of a base; thus, with hydrofluoric, hydrochloric, and hydrobromic acids, it forms compounds. The formula of the hydrochloric compound is given as the type of the rest,

$$As\left\{\begin{array}{l} C_2H_3 \\ C_2H_3 \\ H\,O_2 \\ H\,O_2 \\ \;Cl \end{array}\right.$$: the hydrobromate reacts perfectly neutral.

1154. The cacodylates have the formula, $As\left\{\begin{array}{c} C_2H_3 \\ C_2H_3 \\ O \\ O \\ M\,O_2 \end{array}\right.$

Sulphocacodylic acid has not yet been isolated, but its salts present the same relations to those of cacodylic acid as salts of sulphur acids generally bear to those of oxyacids.

1155. The inorganic models for the tellurium series are chloride of tellurium and tellurous acid,—

$$Te_2\left\{\begin{array}{l} Cl \\ Cl \end{array}\right. \qquad Te_2\left\{\begin{array}{l} O \\ O \\ O \\ O \end{array}\right.$$

The following bodies belonging to the tellurium series are known:—

Tellurium-methyl - - - $Te_2\left\{\begin{array}{l} C_2H_3 \\ C_2H_3 \end{array}\right.$

Tellurous dimethoxide - - $Te_2\left\{\begin{array}{c} C_2H_3 \\ C_2H_3 \\ O \\ O \end{array}\right.$

Tellurous methoxychloride - -	$Te_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\O\\Cl\end{matrix}\right.$
Tellurous dimethiodide - -	$Te_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\I\\I\end{matrix}\right.$
Tellurium ethyl - - - -	$Te_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.$
Tellurous diethoxide - - -	$Te_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\O\\O\end{matrix}\right.$
Tellurous diethosulphide - -	$Te_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\S\\S\end{matrix}\right.$
Tellurous diethochloride - -	$Te_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\Cl\\Cl\end{matrix}\right.$
Tellurous diethoxychloride - -	$Te_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\O\\Cl\end{matrix}\right.$
Tellurous diethiodide - - -	$Te_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\I\\I\end{matrix}\right.$
Tellurium-amyl - - - -	$Te_2\left\{\begin{matrix}C_{10}H_{11}?\\C_{10}H_{11}?\end{matrix}\right.$

The compounds of the alcohol radicals with tellurium are volatile liquids of most unbearable odour. They oxidize readily in contact with air, forming the respective oxides. Tellurium-amyl has not yet been obtained in a state of purity.

The oxides of these bodies are powerful bases, expelling ammonia from its salts, and attracting carbonic acid from the air. They form salts of considerable stability, which, as well as the oxides themselves, yield the original organo-tellurium compounds when treated with sulphurous acid:—

$$Te_2\left\{\begin{matrix}C_4H_5\\C_4H_5\\O\\O\end{matrix}\right. + S_2O_4 = Te_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right. + S_2O_6$$

1156. Viewing these different organo-metallic bodies as framed on the inorganic types we have named, it is interesting to notice the effect which the substitution of positive for negative radicals has upon the properties of the compound. Thus, tribasic arsenic acid, when an atom of methyl has been substituted for oxygen, becomes transformed by the substitution into a bibasic acid, monomethylarsenic acid, $As\left\{\begin{matrix}C_2H_3\\O\\O\\O\\O\end{matrix}\right.$, a well-defined acid of considerable energy, though inferior in chlorous power to arsenic acid. When a second equivalent of oxygen is replaced by methyl, the compound produced is still an acid, cacodylic acid, $As\left\{\begin{matrix}C_2H_3\\C_2H_3\\O\\O\\O\end{matrix}\right.$, but so feeble that it is incapable of forming an ammonia salt. When a third equivalent of oxygen has been replaced by methyl, the compound produced, arsenic trimethoxide, $As\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\O\\O\end{matrix}\right.$ is a feeble biacid base. When a fourth equivalent of oxygen is exchanged for methyl, the compound produced, oxide of tetramethylarsonium, $As\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3,\\C_2H_3\\O\end{matrix}\right.$ is a base of such energy as to be comparable with the caustic alkalies themselves. Such substitutions, Frankland observes, afford striking evidence of the dependence of the chemical character of a compound upon that of each individual constituent.

1157. These organo-metallic bodies are distinguished, as the student will have noticed in reading the description of their properties, for the extraordinary energy of their affinities. Their disposition to unite with negative elements increases with the positive character of the metal, and with the smallness of the atomic weight of the alcohol radical. Thus, organo-potassium and sodium compounds possess more chemical energy than those of zinc; whilst the latter are more active than the compounds of arsenic, antimony, tin, or lead. Again, in the series belonging to each metal, the methylic compounds are more energetic than the ethylic ones, whilst the latter greatly surpass the amylic compounds in this respect.

1158. We have already stated that Frankland considers that the elements are capable of uniting with only a certain number of atoms of other radicals, and this number is definite and unalterable, no matter what may be the character of the uniting atoms. Frankland calls this the extreme stage of combination,—the atomic saturation of the element. We will now illustrate this view that bodies cannot, after they have reached the stage of atomic saturation, combine with a further quantity of an element, by a few examples. The organo-zinc compounds, we have said, are founded on the model of its chloride, $\mathrm{M_2}\left\{\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right.$; they are therefore saturated bodies, and consequently cannot play the part of radicals by combining with other bodies. When they are acted upon, they are decomposed into other and entirely different bodies.

$$(1.)\quad \mathrm{Zn_2}\left\{\begin{matrix}\mathrm{C_2H_3}\\\mathrm{C_2H_3}\end{matrix}\right. + \mathrm{I_4} = 2\,\mathrm{Zn\,I} + 2\left.\begin{matrix}\mathrm{C_2H_3}\\\mathrm{I}\end{matrix}\right\}$$

$$(2.)\quad \mathrm{Zn_2}\left\{\begin{matrix}\mathrm{C_2H_3}\\\mathrm{C_2H_3}\end{matrix}\right. + \mathrm{O_4} = 2\left(\left.\begin{matrix}\mathrm{C_2H_3}\\\mathrm{Zn}\end{matrix}\right\}\mathrm{O_2}\right)$$

Stannic methide, $\mathrm{Sn_2}\left\{\begin{matrix}\mathrm{C_2H_3}\\\mathrm{C_2H_3}\\\mathrm{C_2H_3}\\\mathrm{C_2H_3}\end{matrix}\right.$, and stannic ethide, are in a state of saturation; they are incapable of direct combination. No body can act upon them without expelling one equivalent or more of the positive radical. Thus, when iodine acts upon them, one equivalent of that metalloid is substituted for one equivalent of the alcohol radical, which when liberated combines with an equivalent of the iodine.

$$Sn_2 \left\{ \begin{matrix} C_2H_5 \\ C_2H_5 \\ C_2H_5 \\ C_2H_5 \end{matrix} \right. + I_2 = Sn_2 \left\{ \begin{matrix} C_2H_5 \\ C_2H_5 \\ C_2H_5 \\ I \end{matrix} \right. + \left. \begin{matrix} C_2H_5 \\ I \end{matrix} \right\}$$

The case is different with the stannous compounds. These compounds can combine with a further number of atoms; they become transformed by the combination into stannic compounds.

$$Sn_2 \left\{ \begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix} \right. + O_2 = Sn_2 \left\{ \begin{matrix} C_4H_5 \\ C_4H_5 \\ O \\ O \end{matrix} \right.$$

Organo-metallic bodies, in a state of saturation, do not, as we see by these examples, perform the part of compound radicals; they never undergo change without chemical decomposition. But in the state of partial saturation they play the part of radicals, and they are uniatomic, biatomic, teratomic, or quadratomic, according to the number of molecules requisite to complete their saturation.

1159. "In the combinations of polyatomic metals, we frequently notice, from the lowest to the highest compound, one or more intermediate points of exalted stability. Thus antimony has a teratomic stage of comparative stability. Nitrogen, phosphorus, and arsenic, whilst exhibiting a similar teratomic stage, have also a biatomic one, though of greatly inferior stability; whilst the existence of protoxide of nitrogen, and the recent researches of Griess, render it evident that nitrogen has a third and uniatomic stage.

1160. "In bodies possessing at least one stage of stability below saturation, and in which all the atoms united with the polyatomic element are of the same kind, the stage of maximum stability is very rarely that of saturation.

Thus, in nitrogen, arsenic, and bismuth, compounds of the kind just mentioned, the stage of maximum stability is decidedly the teratomic one. In antimonial compounds of a similar nature, the teratomic is also, though less decidedly, the stage of maximum stability; whilst in phosphorus compounds the points of maximum stability and of saturation generally coincide. When, however, the atoms united with the polyatomic elements are not of the same kind, then the stage of maximum stability usually coincides with that of saturation. Thus the binoxide or bichloride of triethylarsine or triethyl-stibine, are more stable than triethylarsine or triethyl-stibine themselves; but this pentatomic stability reaches its climax in arsonium, stibonium, and phosphonium compounds, as it does also in the corresponding compounds of nitrogen, although the latter element exhibits a much stronger tendency towards universal teratomic stability than its chemical associates.

1161. "In polyatomic organo-metallic bodies, it is remarkable that, with few exceptions, the positive hydrocarbons hold their position much more tenaciously than the associated negative constituents; and we thus frequently find the former accompanying the metal through a vast number of compounds. Hence the group formed by the metal and positive hydrocarbons, has come to be regarded as a compound radical. Thus cacodyl is conceived to be the radical of the whole series of cacodyl compounds. But however great may be the convenience of this mode of viewing organo-metallic compounds, it is a purely artificial distinction, which has no real existence, either in the case of organo-metallic bodies, or, as I shall endeavour to show, in that of organic bodies in general.

1162. "A close examination of the habits of the so-called organo-metallic radicals, shows clearly that their atomic power depends upon their position with regard to the stages of stability and maximum saturation. Thus they are uniatomic when the number of positive groups is one less than that required to reach either the maximum saturation of the metal, or a lower stage of stability. Cacodyl and tetramethyl-arsonium, for instance, are uniatomic radicals, because they are respectively one atom short of the stage of stability and of maximum saturation.

Uniatomic stage.

$$As\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.$$

Cacodyl.

Stage of stability.

$$As\left\{\begin{matrix}C_2H_3\\C_2H_3\\Cl\end{matrix}\right.$$

Chloride of cacodyl.

Uniatomic stage.

$$As\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right.$$

Tetramethylarsonium.

Stage of maximum saturation.

$$As\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\\Cl\end{matrix}\right.$$

Chloride of tetramethylarsonium.

1163. "It is obvious that a compound radical, the number of whose positive atoms is below that of a stage of stability, can have a double atomic character. Thus cacodyl is sometimes uniatomic, as in oxide of cacodyl; and sometimes teratomic, as in cacodylic acid. Again, arseniomonomethyl, As (C_2H_3), is biatomic in arsenious dioxymethide,—

$$As\left\{\begin{matrix}C_2H_3\\O\\O\end{matrix}\right.$$

and quadratomic in monomethylarsenic acid,—

$$As\left\{\begin{matrix}C_2H_3\\O\\O\\O\\O\end{matrix}\right.$$

1164. "If these views of the constitution and character of organo-metallic bodies and their compounds be correct, their application to the organic compounds of carbon becomes inevitable. Regarded from this point of view, the double atom of carbon, like that of tin, is quadratomic in perchloride of carbon and carbonic acid,—

Perchloride of carbon.

$$C_2\left\{\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right.$$

Carbonic acid.

$$C_2\left\{\begin{matrix}O\\O\\O\\O\end{matrix}\right.$$

and biatomic in protochloride of carbon and carbonic oxide,—

Protochloride of carbon. Carbonic oxide.

$$C_2\left\{\begin{matrix}Cl\\Cl\end{matrix}\right. \qquad\qquad C_2\left\{\begin{matrix}O\\O\end{matrix}\right.$$

In other words, the quadratomic stage in carbon compounds is the stage of maximum saturation, whilst the biatomic stage is one of exalted stability. If we substitute an atom of chlorine in perchloride of carbon by one of ethyl, we produce a body having the formula of trichlorhydrine,—

$$C_2\left\{\begin{matrix}C_4H_5\\Cl\\Cl\\Cl\end{matrix}\right.$$

If now a second atom of chlorine be substituted by one of hydrogen, we have a body exhibiting the composition of bichloride of propylene,—

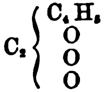
$$C_2\left\{\begin{matrix}C_4H_5\\H\\Cl\\Cl\end{matrix}\right.$$

This view of the constitution of bichloride of propylene renders its relations to allyl and glycerin compounds at once simple and intelligible.

The substitution of a third atom of hydrogen gives the formula of chloride of propyl,—

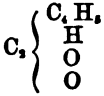
$$C_2\left\{\begin{matrix}C_4H_5\\H\\H\\Cl\end{matrix}\right.$$

whilst the substitution of the last atom of chlorine by hydrogen yields hydride of propyl, and its replacement by ethyl yields the so-called double radical, ethyl-propyl. It still remains for experiment to produce these bodies from perchloride of carbon, and to show that they are identical with the known compounds possessing the same per-centage composition. If, however, we turn to the oxygen compounds of carbon, we are not entirely without experimental evidence of the correctness of this view. Since one atom of oxygen in carbonic acid has been replaced by ethyl, with production of the body theoretically indicated, namely, propionic acid,—



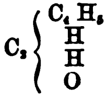
$$C_2\left\{\begin{array}{l}C_4H_5\\O\\O\\O\end{array}\right.$$

could a second atom of oxygen be substituted by hydrogen, we ought to produce propionic aldehyde,—



$$C_2\left\{\begin{array}{l}C_4H_5\\H\\O\\O\end{array}\right.$$

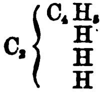
The replacement of a third atom of oxygen by hydrogen would then yield propylic ether,—



$$C_2\left\{\begin{array}{l}C_4H_5\\H\\H\\O\end{array}\right.$$

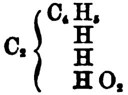
whilst the replacement of the last atom of oxygen by hydrogen should give rise to hydride of propyl, and by uniatomic peroxide of hydrogen, to propylic alcohol,—

Hydride of propyl.



$$C_2\left\{\begin{array}{l}C_4H_5\\H\\H\\H\end{array}\right.$$

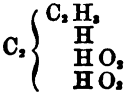
Propylic alcohol.



$$C_2\left\{\begin{array}{l}C_4H_5\\H\\H\\HO_2\end{array}\right.$$

1165. The glycols are also constructed upon the carbonic acid type,—

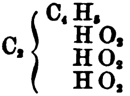
Glycol.



$$C_2\left\{\begin{array}{l}C_2H_3\\H\\HO_2\\HO_2\end{array}\right.$$

and to the same type belongs also the teracid alcohol, glycerin,—

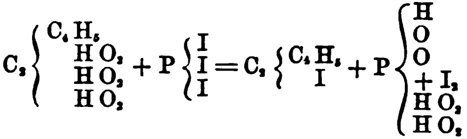
Glycerin.



$$C_2\left\{\begin{array}{l}C_4H_5\\ \quad HO_2\\ \quad HO_2\\ \quad HO_2\end{array}\right.$$

Under the influence of iodide of phosphorus, glycerin yields iodide of allyl,—

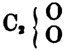
Glycerin.



$$C_2\left\{\begin{array}{l}C_4H_5\\ \quad HO_2\\ \quad HO_2\\ \quad HO_2\end{array}\right. + P\left\{\begin{array}{l}I\\ I\\ I\end{array}\right. = C_2\left\{\begin{array}{l}C_4H_5\\ \quad I\end{array}\right. + P\left\{\begin{array}{l}H\\ O\\ O\\ +I_3\\ HO_2\\ HO_2\end{array}\right.$$

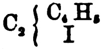
Here we have a reduction from the carbonic acid to the carbonic oxide type, of precisely the same nature as that which occurs when cacodylic acid is reduced to oxide of cacodyl. Allylic compounds are therefore constructed upon the carbonic oxide type.

Carbonic oxide.



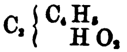
$$C_2\left\{\begin{array}{l}O\\ O\end{array}\right.$$

Iodide of allyl.



$$C_2\left\{\begin{array}{l}C_4H_5\\ \quad I\end{array}\right.$$

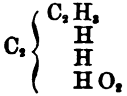
Allylic alcohol.



$$C_2\left\{\begin{array}{l}C_4H_5\\ \quad HO_2\end{array}\right.$$

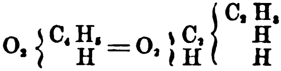
1166. "It would be easy greatly to extend this view of the constitution of organic carbon compounds; but the above examples are sufficient to indicate its general application somewhat more fully than I have previously done; and more than this is not desirable, until the hypothesis has been further supported by experimental results.

1167. "In conclusion, it is evident that this is only one mode of applying to organic compounds the law of chemical combination, which I have endeavoured to deduce from the constitution and behaviour of organo-metallic bodies. Its application ought to be, and will be found to be, equally truthful in referring organic compounds containing hydrogen, oxygen, or nitrogen, to the inorganic typical compounds of each of these elements. Thus, for example, we can represent alcohol,—1st, as derived from carbonic acid,—



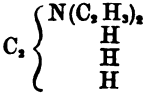
$$C_2\left\{\begin{matrix}C_2H_3\\H\\H\\HO_2\end{matrix}\right.$$

2nd, as derived from water,—



$$O_2\left\{\begin{matrix}C_4H_5\\H\end{matrix}\right. = O_2\left\{\begin{matrix}C_2\\H\end{matrix}\right.\left\{\begin{matrix}C_2H_3\\H\\H\end{matrix}\right.$$

1168. "In like manner, nitrogen compounds and their analogues, whilst derived from typical inorganic compounds of nitrogen, are also true derivatives from the carbon types. Thus, trimethylamine is correctly written as a derivative from carbonic acid,—



$$C_2\left\{\begin{matrix}N(C_2H_3)_2\\H\\H\\H\end{matrix}\right.$$

1169. "Each of these modes of notation is equally correct; but I conceive that a large number of those organic bodies which are usually formulated in accordance with the water, and hydrochloric acid models, would be much more usefully expressed upon the carbonic acid and carbonic oxide types, and that, as a general rule, organic as well as inorganic compounds are most instructively represented upon the typical compounds of the most polyatomic element they contain. The formulation of organic compounds is not a matter of indifference, even to the chemical investigator; and hence every mode of expression founded upon broad chemical relations, ought to have the preference over more purely artificial methods.[*]

1170. *Dr. Kolbe's views.*—Nature, Kolbe believes, has not limited herself to form all natural organic bodies on the four types which Gerhardt has selected. This is amply confirmed, Dr. Kolbe thinks, by the unnatural efforts which Gerhardt's imitators have been obliged to adopt in order to support their system. It has been admitted by them that the four types above mentioned are not sufficient for the production of the vast number of organic compounds of the most heterogeneous qualities, and the most diverse composition. Hence derivative and even mixed types have been assumed, whereby chemistry has with some degenerated into a mere enumeration of formulæ.

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[*] The student is referred, for further information about Frankland's views, to the following papers by that chemist:—

(1.) "On a New Series of Organic Bodies containing Metals."—*Philosophical Transactions*, 1852.

(2.) "On the Production of Organic Bodies without the Agency of Vitality."—*Journal of Royal Institution*," part viii., 1858.

(3.) "Organo-Metallic Bodies."—*Quarterly Journal Chemical Society*.

1171. By the derivation of all organic compounds from four types, the former are artificially brought into mere external relations to the inorganic compounds. There really exists between both, Kolbe thinks, a much closer natural connection, to which, in his opinion, sufficient attention has as yet not been paid. This connection does not consist simply in the similar elementary composition of organic substances, nor in their both following the laws of chemical combination, but is based on relations of affinity. *The organic bodies of chemistry are the direct results of inorganic combinations, and are formed from the latter by marvellously simple processes of substitution.*

1172. Kolbe then proceeds to show the true connection, according to his opinion, which exists between organic and inorganic compounds. He considers, as the student will see, that the fatty and other acids, the alcohols, aldehydes, acetones, and hydrocarbons, are all derived from carbonic acid.

1173. When, in carbonic acid (C_2O_4), one of the four atoms of oxygen is exchanged for an atom of hydrogen, formic acid* is produced; and when two other atoms of oxygen are replaced by hydrogen, methylic alcohol,—

$$C_2O_4 \qquad HO, C_2\left\{\begin{matrix} H \\ O_3 \end{matrix}\right. \qquad HO, C_2\left\{\begin{matrix} H_3 \\ O \end{matrix}\right.$$

1174. Dr. Kolbe prefers placing to the left of the symbol for the radical the positive elements which are substituted for oxygen, and other negative members of an inorganic combination. The above formulæ will, according to this plan, take the following form:—

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* Since Dr. Kolbe wrote his paper, he has formed formic acid according to this view (see par. 626).

Carbonic acid.	Formic acid.	Methylic alcoho.
$2\,HO, C_2O_4$	HO, HC_2O_3	HO, H_3C_2O

1175. The fact deserves notice that the bibasic carbonic acid, after parting with one atom of oxygen for hydrogen, becomes transformed into a monobasic acid, formic acid; and that oxide of methyl, which is, according to Kolbe's idea, formed by a further substitution of hydrogen for oxygen in carbonic acid, possesses the same capacity of saturation as formic acid. The reason of this is most closely connected with the question, Why is carbonic acid a bibasic acid?

1176. It is evident the capacity of saturation of carbonic and other acids depends on the number of oxygen atoms which stand outside the respective radicals; and they require as many atoms of monacid bases for their neutralization as they contain atoms of oxygen outside the radicals. The same law applies equally to the bases.

1177. Nitric acid is a monobasic acid, because it is the monoxide of the radical NO_4. Sulphuric acid is a bibasic acid, because it has two atoms of oxygen conjoined with the radical S_2O_4; and phosphoric acid is tribasic, because only two out of its five atoms of oxygen belong to the radical. It becomes converted into bibasic and monobasic phosphoric by one and two atoms of oxygen outside the radical entering into the radical, thereby forming new radicals, richer in oxygen.

$3\,HO, (PO_2)\,O_3$ - - tribasic phosphoric acid
$2\,HO, (PO_3)\,O_2$ - - bibasic ,, ,,
$HO, (PO_4)\,O$ - - monobasic ,, ,,

1178. In like manner, carbonic acid is a bibasic acid, because it contains two atoms of oxygen conjoined with the radical carbonyl $(C_2O_2)\,O_2$. It is probable that, as in the case of phosphoric acid, there exists besides the bibasic carbonic acid, another isomeric but monobasic acid of the composition $HO\,(C_2O_3)\,O$; perhaps, also, a tribasic one, $3\,HO\,(C_2O)\,O_3$, of which latter we find derivatives in oxhydrate of lipyl, and many other compounds.

1179. The transformation of a polybasic acid into one of inferior saturating capacity may take place in another manner. We find that a diminution of the capacity for saturation always follows when one or more of the atoms of oxygen outside the radical is replaced by heterogeneous elements. In this case phosphoric acid is also the best example; by an exchange of one or two atoms of oxygen for as many of hydrogen, it becomes converted into the bibasic or monobasic acid, thus:—

$3\,H\,O, (P\,O_2)\,O_3$ - - tribasic phosphoric acid
$2\,H\,O, H\,(P\,O_2)\,O_2$ - bibasic „ „
$H\,O, 2\,H\,(P\,O_2)\,O$ - monobasic „ „

1179. In the same way the monobasic sulphate of acid methyl, sulphate of phenyl, &c., are derived from bibasic sulphuric acid; and bibasic carbonic passes, from similar causes, into monobasic, formic acid, acetic acid, &c.

$2\,H\,O, (C_2\,O_2)\,O_2$ - - - carbonic acid
$H\,O, H\,(C_2\,O_2)\,O$ - - - formic acid
$H\,O, (C_2\,H_3)\,(C_2\,O_2)\,O$ - - acetic acid.

If this substitution extends to the second atom of oxygen, the acid nature disappears. The resulting compounds, aldehyde and acetone, no longer unite with bases to form salts.

1180. If by further substitution one of the two atoms of oxygen in the radical is exchanged for hydrogen, so that of the four original atoms in the atom of carbonic acid three are replaced by an equal number of atoms of hydrogen, the remaining atom of oxygen goes quite out of the radical, and we then have the monoxide of a new mono-atomic radical, methyl, $H_3\,C_2$, which stands to hydrogen in a perfectly analogous relation. If, finally, the fourth atom of oxygen in the carbonic acid atom be replaced by hydrogen, pit gas is formed, which may accordingly be regarded as the hydrogen compound of methyl. The different phases of these substitutions are properly expressed by the following formulæ:—

$2\,H\,O, (C_2\,O_2)\,O_2$ - carbonic acid
$H\,O, H\,(C_2\,O_2)\,O$ - formic acid
$H_2\,(C_2\,O_2)$ - - an as yet unknown aldehyde
$H\,O\,(H_3\,C_2)\,O$ - methylic alcohol
$H_4\,C_2$, or $H_3\,C_2, H$ pit gas.

1181. If we substitute methyl instead of hydrogen for the oxygen of the carbonic acid, we form, 1st, acetic acid, then acetone; and if we substitute some of the oxygen by hydrogen, we form aldehyde, vinic alcohol, &c., as shown in the following table:—

$2HO, (C_2O_2)O_2$	carbonic acid
$HO, (C_2H_3)(C_2O_2)O$	acetic acid
$\left(\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right)(C_2O_2)$	acetone
$\left(\begin{matrix}C_2H_3\\H\end{matrix}\right)(C_2O_2)$	aldehyde
$HO, \left(\begin{matrix}C_2H_3\\H_2\end{matrix}\right)C_2, O$	vinic alcohol
$\begin{matrix}C_2H_3\\H_3\end{matrix}, C_2$	hydride of ethyl.

1182. If we thus replace the oxygen atoms of carbonic acid by the different alcohol radicals and hydrogen, we should form the whole series of fatty acids and their aldehydes, acetones, alcohols, and hydrocarbons; and we see strong reasons for believing that from these combinations we might ascend to the formation of starch, sugar, gum, and other vegetable productions. The first thing to be done is to find out a method of converting the fatty acids directly into their alcohols. No method is at present known by which we can effect this transformation.

1183. The fatty acids, their aldehydes, acetones, alcohols, hydrocarbons, may, according to their composition and their relationship to carbonic acid, be characterised as follows:—

1184. The fatty, aromatic, and allied monobasic acids are derivatives of carbonic acid, arising from the substitution of hydrogen or an alcohol radical for one of the two extra-radical oxygen atoms.

1185. Acetones are those derivatives of carbonic acid in which both the extra-radical oxygen atoms have been replaced by alcohol radicals. Aldehydes are the derivatives of carbonic acid in which one of the two extra-radical atoms of oxygen have been replaced by an alcohol radical, and the other atom has been replaced by hydrogen.

1186. Alcohols are the derivatives of carbonic acid in which three of the oxygen atoms are replaced, one by an alcohol radical, the other two by an equal number of atoms of hydrogen. These derivative bodies are united with an atom of water to form the alcohols. Only in methyl alcohol are all the three oxygen atoms replaced by an equal number of hydrogen atoms.

1187. In the corresponding hydrocarbons all the oxygen in the carbonic acid is replaced by positive radicals, three of the atoms being replaced by an equal number of hydrogen atoms, and the other atom by an alcohol radical. Only in pit gas are all the four atoms of oxygen replaced by an equal number of hydrogen atoms.

1188. If attention be paid to the formulæ by which I have expressed the rational composition of acetic acid of the aldehydes and alcohols, viz.:—

$$HO, (C_2H_3)(C_2O_2)O \quad - \quad - \quad - \quad \text{acetic acid}$$

$$\left(C_2 \genfrac{}{}{0pt}{}{H_3}{H}\right)(C_2O_2) \quad - \quad - \quad - \quad - \quad \text{aldehyde}$$

$$HO, \left(C_2 \genfrac{}{}{0pt}{}{H_3}{H_2}\right)(C_2O) \quad - \quad - \quad - \quad \text{alcohol,—}$$

it will be seen at a glance how it is that in the oxidation of alcohol out of the five hydrogen atoms in oxide of ethyl only two atoms of hydrogen are replaced; and that in the oxidation of aldehyde only one atom of hydrogen is replaced. It is those atoms of hydrogen in alcohol and aldehyde that stand alone which yield to the oxidizing influences, and are much more assailable by oxygen than the more tenaciously combining hydrogen atoms in the methyl radical.

1189. The above view of the chemical constitution of the alcohols affords us hopes of the discovery of new and as yet unknown alcohols, as well as of a new class of substances nearly related to the alcohols in composition, sharing with them, as may be expected, many properties, but differing from them in many essential points.

1190. As soon as we possess the means of changing all alcoholic acids by direct introduction of one or two atoms of hydrogen in the place of as many atoms of oxygen, we shall then not only be able to form the ordinary aldehydes and alcohols, but we may expect to form corresponding alcohols and aldehydes from the derivatives of the primary acids, as amido-acetic acid, oxyacetic acid, &c. The following comparative table of the formulæ in question will best exhibit these relations:—

Acetic acid. Aldehyde of acetic acid. Alcohol.

$$HO, (C_2H_3)(C_2O_2)O\,;\quad \left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}(C_2O_2;\quad HO\left\{\begin{matrix}C_2H_3\\H_2\end{matrix}\right\}C_2O$$

Amido-acetic acid. Aldehyde of amido-acetic acid.

$$HO,\left(C_2\left\{\begin{matrix}H_2\\H_2N\end{matrix}\right.\right)(C_2O_2)O\qquad \left(C_2\left\{\begin{matrix}H_2\\H_2N\\H\end{matrix}\right.\right)(C_2O_2)$$

Alcohol of amido-acetic acid.

$$HO,\left(C_2\left\{\begin{matrix}H_2\\H_2N\\H_2\end{matrix}\right.\right)C_2O$$

Oxyacetic acid. Aldehyde of oxyacetic acid.

$$HO,\left(C_2\left\{\begin{matrix}H_2\\HO_2\end{matrix}\right.\right)(C_2O_2)O\qquad \left(C_2\left\{\begin{matrix}H_2\\HO_2\\H\end{matrix}\right.\right)(C_2O_2)$$

Alcohol of oxyacetic acid.

$$HO,\left(C_2\left\{\begin{matrix}H_2\\HO_2\\H_2\end{matrix}\right.\right)C_2O$$

1191. If, in an aldehyde, the independent hydrogen atom be replaced by compound radicals, acetones are produced.

$$\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}(C_2O_2)\ \text{aldehyde}$$

$$\left.\begin{matrix}\left.\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\}(C_2O_2\\ \left.\begin{matrix}C_2H_3\\C_4H_5\end{matrix}\right\}C_2O_2\end{matrix}\right\}\text{acetones.}$$

Let us suppose that, in like manner, in the alcohols one or both of the independent hydrogen atoms be replaced by as many atoms of methyl, ethyl, &c., the results are new alcoholic compounds of the following composition:—

$$HO\left\{\begin{matrix}C_2H_3\\H_2\end{matrix}\right\}C_2O,\ \text{normal alcohol}$$

$$HO\left\{\begin{matrix}C_2H_3\\C_2H_3\\H\end{matrix}\right\}C_2O,\ \text{methylized alcohol}$$

$$HO\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right\}C_2O,\ \text{bimethylized alcohol}$$

$$HO\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_4H_5\end{matrix}\right\}C_2O,\ \text{methyl-ethylized alcohol.}$$

1192. The methylized alcohol would be isomeric—not identical—with propylic alcohol.

$$HO\left\{\begin{matrix}C_2H_3\\C_2H_3\\H\end{matrix}\right\}C_2O,\ \text{methylized alcohol}$$

$$HO\left\{\begin{matrix}C_4H_5\\H_2\end{matrix}\right\}C_2O,\ \text{propylic alcohol.}$$

Bimethylized alcohol would be isomeric—not identical—with butylic alcohol.

1193. Although none of these alcoholic bodies have yet been produced, it is possible to predict their chemical action in many points. It may be expected that they will form haloid compounds with the hydrogen acids, like the normal alcohols; and that they will form sulphur compounds, mercaptans, and bodies analogous to sulphovinic acid. But the bodies formed like bimethylized alcohol will not, like the normal alcohols, be transformed, by means of oxidation, into aldehydes and acids, as they have not those two independent atoms of hydrogen on which, in normal alcohols, oxidation is effected. The bodies like methylized alcohol, which contain an independent atom of hydrogen, will not furnish acids by oxidation, but will furnish by oxidation acetones.

$$\overset{\text{Methylized alcohol.}}{HO\left\{\begin{matrix}C_2H_3\\C_2H_3\\H\end{matrix}\right\}C_2O}+2O=\overset{\text{Acetone.}}{\left.\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\}C_2O_2}$$

Perhaps to this class of bodies may be referred the oxhydrate of phenyl, and the analogous alcoholic compounds, which, in many respects, are analogously related to the normal alcohols, but are essentially distinguished from them by their not admitting of a transformation into aldehydes and acids. It is probable that the oxyhydrate of cresyl, $HO_2, C_{14}H_7O$, stands to the isomeric oxhydrate of toluyl in the same relation as the supposed bimethylized alcohol to the isomeric butylic alcohol.

1194. The substitution of positive radicals for the oxygen in carbonic acid may take place in another way. Let us suppose that in the group of atoms $(C_2O_2)O_2$, the oxygen atoms of the radical, and not the extra-radical atoms, are replaced by hydrogen, methyl, &c., the result will be the formation of the bibasic or biacid compounds discovered by Wurtz, whose hydrates are called glycols. These glycols are formed out of ethylene and other homologous hydrocarbons.

1195. These hydrocarbons may be conceived to be derived from carbonic oxide (C_2O_2) by the replacement of one atom of oxygen by hydrogen, and the replacement of the other atom of oxygen by a compound radical, like methyl. These relations are clearly seen in the following comparison of the formulæ in question:—

$$C_2O_2, \text{ carbonic oxide}$$

$$\left.\begin{matrix} C_2H_3 \\ H \end{matrix}\right\} C_2, \text{ ethylene.}$$

As in their composition, so also in their chemical action, carbonic oxide (carbonyl) and ethylene agree unmistakeably. Both are biatomic radicals; both unite themselves directly with two atoms of chlorine; both also, under favorable circumstances, unite with two atoms of oxygen; both assimilate the elements of one atom of water, carbonic oxide in the presence of an alkali, giving rise thereby to formic acid and ethylene in the presence of sulphuric acid, forming oxide of ethyl.

1196. This union of carbonic oxide and ethylene with water does not, as is evident from the composition of formic acid and oxide of ethyl, take place by the water, as such, entering unchanged into the combination, but by a separation of its component parts, and entrance of hydrogen into the said radical, whence result from biatomic carbonic oxide and ethylene respectively, the monatomic radicals, formyl-oxyl, $H(C_2O_2)$, and ethyl, $\left.\begin{matrix} C_2H_3 \\ H_2 \end{matrix}\right\} C_2$. Carbonic oxide and ethylene act differently when they unite with chlorine and oxygen. When they combine with these elements, their diatomic character is retained in the new compound, for the two additional atoms of Cl or oxygen stand outside the radical. Examples: $(C_2O_2)\,O_2$, oxide of ethylene, $\left(C_2\left\{\frac{C_2H_3}{H}\right.\right)O_2$,—and therefore they must, according to the law already stated, be bibasic and biacid respectively.

1197. The reason why oxide of ethylene and isomeric aldehyde have different properties, and are, on the whole, quite different substances, is simply this,—that the first contains the two oxygen atoms outside the radical; the second, the two oxygen atoms within the radical, replaced respectively by an atom of methyl and hydrogen, as is symbolically expressed by the following formulæ:—

$(C_2O_2)\frac{C_2H_3}{H}$, aldehyde

$(C_2Cl_2)\,C_2\frac{H_3}{H}$, chloride generated from aldehyde by PCl_5

$\left(C_2\left\{\frac{C_2H_3}{H}\right.\right)O_2$, oxide of ethylene

$\left(C_2\left\{\frac{C_2H_3}{H}\right.\right)Cl_2$, chloride of ethylene.

1198. In acrylic acid, in the acids of the oleic series, and in cinnamic acid, an atom of a radical, C_4H_3, is substituted for an atom of the hydrogen in the substituted radical in fatty acid and benzoic series, thus:—

Benzoic acid.	Cinnamic acid.
$HO,(C_{12}H_5)(C_2O_2)O$	$HO\left(C_{12}\left\{\frac{H_4}{C_4H_3}\right.\right)(C_2O_2)O$

1199. Kolbe considers that the bibasic acids of the succinic acid series, and similarly constituted bibasic acids, are derived from two atoms of carbonic acid, in which two out of the four extra-radical atoms of oxygen are replaced by some member of the ethylene family of diatomic radicals, thus:—

Double atom of carbonic acid.	Succinic acid.
$\left(\begin{matrix}C_2O_2\\C_2O_2\end{matrix}\right)O_4$	$2HO,(C_4H_4)''\left(\begin{matrix}C_2O_2\\C_2O_2\end{matrix}\right)O_2$

If we subtract from these biatomic acids an atom of carbonic acid, we obtain the monatomic alcohol acids, thus:—

Succinic acid. Propionic acid.

$$2\,HO,(C_4H_4)\begin{pmatrix}C_2O_2\\C_2O_2\end{pmatrix}O_2 - C_2O_4 = HO,C_4H_5(C_2O_2)O$$

1200. This transformation, Kolbe thinks, may probably be effected by heating the bibasic acids along with hydrate of potash in excess, up to a definite temperature, which must of course be lower than that at which the monobasic acids, which are supposed to result, would be themselves decomposed by the potash.* Perhaps these bibasic acids, in the first stage of their transformation, might assimilate the elements of an atom of water, and thus become converted into tribasic acids; thus, succinic acid would become $3\,HO,(C_4H_5)\begin{pmatrix}C_2O_2\\C_2O_2\end{pmatrix}O_3$, which in the second stage of decomposition, at an increased temperature, might separate into propionic acid and carbonic acid.

1201. Kolbe supposes that citric acid and aconitic acid are derived from three atoms of carbonic acid, in which three out of the six extra-radical atoms of oxygen are replaced by a teratomic radical.

1202. Of the organic derivatives of sulphuric acid, Kolbe remarks, there have hitherto been known almost only those which stand to it in the same relation as the alcohol acids, the acetones, and the acids analogous to succinic acid stand, in respect to their composition, to carbonic acid. He shows, by the following examples, that there is a correspondence between the derivatives of carbonic acid and sulphuric acid.

Carbonic acid.	Sulphuric acid.
$(C_2O_2)O_2$	$(S_2O_4)O_2$
Propionic acid.	Ethyl-sulphuric acid.
$HO,(C_4H_5)(C_2O_2)O$	$HO,(C_4H_5)(S_2O_4)O$
Propione.	Unknown.
$\begin{pmatrix}C_4H_5\\C_4H_5\end{pmatrix}(C_2O_2)$	$\begin{pmatrix}C_4H_5\\C_4H_5\end{pmatrix}(S_2O_4)$
Chlor-propionic acid.	Chlorethyl-sulphuric acid.
$HO,\left(C_4\left\{\begin{matrix}H_4\\Cl\end{matrix}\right.\right)(C_2O_2)O$	$HO,\left(C_4\left\{\begin{matrix}H_4\\Cl\end{matrix}\right.\right)(S_2O_4)O$

---

* Koch has since effected this transformation in the above way.—*Annalen*, 119, p. 173.

Amidopropionic acid (alanine).	Amidoethyl-sulphuric[*] acid (taurine).
$H\,O, \left(C_4 \left\{ \begin{matrix} H_4 \\ H_2N \end{matrix} \right. \right) (C_2O_2)\,O$	$H\,O, \left(C_4 \left\{ \begin{matrix} H_4 \\ H_2N \end{matrix} \right. \right) (S_2O_4)\,O$

---

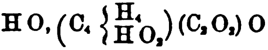
[*] Some years ago, Strecker discovered that isethionate of ammonia, when heated to 210° C., gives off water, and is converted into taurine. Subsequently Gibbs discovered that, when taurine is treated with nitrous acid, it is converted into isethionic acid. These experiments prove the existence of intimate relations between taurine and isethionic acid; but as taurine does not eliminate ammonia when heated along with hydrate of potash *until* it arrives at its melting point, and it is at that temperature completely decomposed, it proves that taurine is not the amide of isethionic acid.

These experiments led Kolbe to the conclusion, which is exhibited in the above table, that taurine is related to isethionic acid in the same manner as alanine to lactic acid; as these last two bodies may be regarded as derivatives of ethyl-carbonic (propionic) acid, alanine as amidoethyl-carbonic acid, and lactic acid as oxyethyl-carbonic acid, so likewise may taurine and isethionic be viewed as derivatives of ethyl-sulphuric acid, viz., taurine as amidoethyl-sulphuric acid, and isethionic acid as oxyethyl-sulphuric acid; these relations are exhibited in the above table.

The following objection might be raised against the assumption that taurine and alanine are so nearly related as these formulæ indicate,—taurine does not possess the power which is common to glycocine, alanine, leucine, aspartic acid, amidobenzoic acid, and amido acids in general, of forming saline compounds, both with bases and with acids. But Kolbe points out that, independently of the fact that the organic derivatives of sulphuric acid differ in many points from those of carbonic acid, the following consideration is of especial importance. It is reasonable to suppose that, by the introduction of amidogen into the ethyl-molecule, the acid properties of ethyl-sulphuric acid will be weakened, as the properties of ethyl-carbonic (propionic) are weakened in alanine. As ethyl-sulphuric acid is a more powerful acid than ethyl-carbonic acid, it is not suprising that the weak basic properties which the amidated propionic acid possesses, are not possessed by amidated ethyl sulphuric acid, but that this possesses weak acid properties. Dr. Kolbe also thought amidated ethyl-sulphuric acid might possess properties which had not hitherto been actually observed in pure taurine; he, therefore, prepared some pure taurine from ox-bile, in order carefully to study its chemical properties. He found from these experiments that taurine cannot combine with acids; that, unlike alanine, it cannot form crystallizable compounds with salts, when its aqueous solution is evaporated with a solution of a salt, say, chloride of potassium; that a solution of it in $H\,Cl$ does not yield a compound with $Pt\,Cl_2$. Although he did not obtain any salts in the solid, he found that taurine is a weak acid, and not, as hitherto supposed, an indifferent body. These experiments show that as the basic properties of aniline are weakened in trichloraniline by the introduction of chlorine, in like manner the acid properties of ethyl-sulphuric acid are weakened in taurine by the substitution of amidogen for hydrogen.

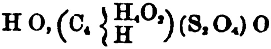
Very recently (since his paper on the classification of bodies was printed) Dr. Kolbe has attempted, with perfect success, to confirm by experiment this conjecture of his, "that taurine is related to isethionic acid, and in the same manner as alanine is to lactic acid." The next important point for the student to learn is, on what suggestion Dr. Kolbe acted in trying to prove his conjecture by experiment. The following was the suggestion;—If isethionic acid be really constituted similarly to lactic acid, as above suggested, it might be expected to exhibit, under the influence of pentachloride of phosphorus, a transformation similar to that of lactic acid, yielding, in fact, the chloride of chlorethyl-sulphuric acid, thus:—

Oxypropionic acid (lactic acid).



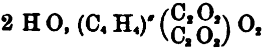
$$HO,\left(C_4\left\{\begin{matrix}H_4\\HO_2\end{matrix}\right.\right)(C_2O_2)O$$

Oxyethyl-sulphuric acid) isethionic acid



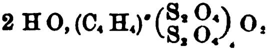
$$HO,\left(C_4\left\{\begin{matrix}H_4O_2\\H\end{matrix}\right.\right)(S_2O_4)O$$

Succinic acid.



$$2\,HO,(C_4H_4)''\begin{pmatrix}C_2O_2\\C_2O_2\end{pmatrix}O_2$$

Disulpethyl acid.



$$2\,HO,(C_4H_4)''\begin{pmatrix}S_2O_4\\S_2O_4\end{pmatrix}O_2$$

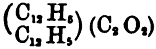
Benzoic acid.

$$HO,(C_{12}H_5)\ (C_2O_2)O$$

Phenyl-sulphuric acid.

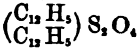
$$HO,(C_{12}H_5)\ (S_2O_4)O$$

Benzophenone.



$$\begin{pmatrix}C_{12}H_5\\C_{12}H_5\end{pmatrix}(C_2O_2)$$

Sulphobenzide.

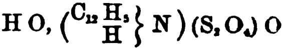


$$\begin{pmatrix}C_{12}H_5\\C_{12}H_5\end{pmatrix}S_2O_4$$

Carbanalid acid.

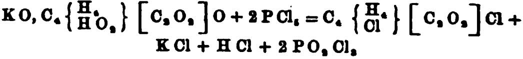
$$HO,\left(\left.\begin{matrix}C_{12}H_5\\H\end{matrix}\right\}N\right)(C_2O_2)O$$

Sulphanalid acid.



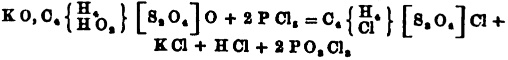
$$HO,\left(\left.\begin{matrix}C_{12}H_5\\H\end{matrix}\right\}N\right)(S_2O_4)O$$

Lactate of potash. Chloride of chloropropionic acid.



$$KO,C_4\left\{\begin{matrix}H_4\\HO_2\end{matrix}\right\}\left[C_2O_2\right]O+2\,PCl_5=C_4\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}\left[C_2O_2\right]Cl+KCl+HCl+2\,PO_2Cl_3$$

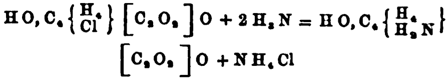
Isethionate of potash. Chloride of chlorethyl-sulphuric acid.



$$KO,C_4\left\{\begin{matrix}H_4\\HO_2\end{matrix}\right\}\left[S_2O_4\right]O+2\,PCl_5=C_4\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}\left[S_2O_4\right]Cl+KCl+HCl+2\,PO_2Cl_3$$

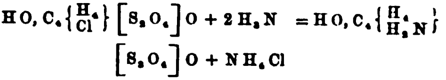
It might further be expected that the chlorethyl-sulphuric acid resulting from the action of water on this chloride, would be converted by appropriate treatment with ammonia, into taurine, just as the analogously constituted compound, chloropropionic acid, is thereby converted into alanine.

(1.)



$$HO,C_4\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}\left[C_2O_2\right]O+2\,H_3N=HO,C_4\left\{\begin{matrix}H_4\\H_2N\end{matrix}\right\}\left[C_2O_2\right]O+NH_4Cl$$

(2.)



$$HO,C_4\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}\left[S_2O_4\right]O+2\,H_3N=HO,C_4\left\{\begin{matrix}H_4\\H_2N\end{matrix}\right\}\left[S_2O_4\right]O+NH_4Cl$$

The results of Kolbe's experiments completely fulfilled these expectations. He obtained, 1st, chloride of chlorethyl-sulphuric acid in the above way: 2nd, he obtained taurine from this compound, by the action of ammonia in the way just indicated.*

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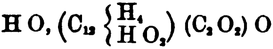
* The student is referred, for further information with regard to these experimental results, to Kolbe's paper in vol. xv., p. 94, *Journal of the Chemical Society.*

Amidobenzoic acid.

$$HO,\left(C_{12}\left\{\begin{matrix}H_4\\H_2N\end{matrix}\right.\right)(C_2O_2)O$$

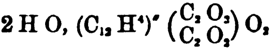
$$HO,\left(C_{12}\left\{\begin{matrix}H_4\\H_2N\end{matrix}\right.\right)(S_2O_4)O$$

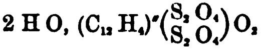
Oxybenzoic acid. Oxyphenyl-sulphuric acid.


$$HO,\left(C_{12}\left\{\begin{matrix}H_4\\HO_2\end{matrix}\right.\right)(C_2O_2)O$$

$$HO,\left(C_{12}\left\{\begin{matrix}H_4\\HO_2\end{matrix}\right.\right)(S_2O_4)O$$

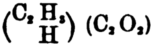
Phthalic acid. Disulphobenzole acid.

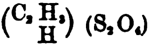

$$2HO,(C_{12}H^4)''\left(\begin{matrix}C_2O_2\\C_2O_2\end{matrix}\right)O_2$$


$$2HO,(C_{12}H_4)''\left(\begin{matrix}S_2O_4\\S_2O_4\end{matrix}\right)O_2$$

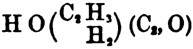
1203. The above comparisons, when further extended, afford hopes of a discovery of different new combinations. It may be assumed, for instance, with tolerable probability, that among the derivatives of sulphuric acid, there exist compounds of the constitution of the aldehydes and alcohols of perhaps the following composition:—

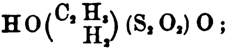
Aldehyde.


$$\left(C_2\begin{matrix}H_3\\H\end{matrix}\right)(C_2O_2)$$

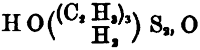

$$\left(C_2\begin{matrix}H_3\\H\end{matrix}\right)(S_2O_4)$$

Alcohol.


$$HO\left(C_2\begin{matrix}H_3\\H_2\end{matrix}\right)(C_2,O)$$


$$HO\left(C_2\begin{matrix}H_3\\H_2\end{matrix}\right)(S_2O_2)O;$$

or,


$$HO\left(\begin{matrix}(C_2H_3)_3\\H_2\end{matrix}\right)S_2,O$$

1204. Dr. Kolbe now regards the compound, which fourteen years ago he described as sulphuric acid and superchloride of carbon ($C\,Cl_2, S\,O_2$), as the derivative of bibasic sulphuric acid, which contains one of the two extra-radical oxygen atoms replaced by trichloride of methyl, the other by an atom of chlorine, viz., $(C_2Cl_3)(S_2O_4)Cl$. He considers that the compound which has been described as the sulphuric acidized chloride of carbon, $C\,Cl, S\,O_2$, and which, on account of its instability, has never been isolated, is the aldehyde of trichlor-methyl-sulphuric acid; its formula would, according to this idea, be $\left(C_2\begin{matrix}Cl_3\\H\end{matrix}\right)(S_2O_4)$. He thinks that the formation and chemical reactions support this view of its constitution.

1204. It has been previously noticed that he considers succinic is derived from two atoms of carbonic acid, 2 H O,

$(C_4H_4)'' \binom{C_2O_2}{C_2O_2} O_2$, and disulphethylic acid from two atoms of sulphuric acid, $2\,HO, (C_4H_4)'' \binom{S_2O_4}{S_2O_4} O_2$: as the double radicals $\binom{C_2O_2}{C_2O_2}$ and $\binom{S_2O_4}{S_2O_4}$ are of equal value, it is evident that no change would take place in the capacity for saturation if in the double radical $\binom{C_2O_2}{C_2O_2}$ one of the two radicals, C_2O_2, were replaced by S_2O_4; there would result a bibasic acid of this composition,—

$$2\,HO, (C_4H_4)'' \binom{C_2O_2}{S_2O_4} O_2$$

There actually exists not only this compound, but a whole series of acids of a similar composition. To these belong,—

Acetic sulphuric acid	-	$2\,HO, (C_2H_2)'' \binom{C_2O_2}{S_2O_4} O_2$
Propionic sulphuric acid		$2\,HO, (C_4H_4)'' \binom{C_2O_2}{S_2O_4} O_2$
Butyric sulphuric acid	-	$2\,HO, (C_6H_6)'' \binom{C_2O_2}{S_2O_4} O_2$
Benzoic sulphuric acid	-	$2\,HO, (C_{12}H_4)'' \binom{C_2O_2}{S_2O_4} O_2$

1205. The above compounds have not, as yet, been produced from the corresponding bibasic acids containing the double radical $\binom{C_2O_2}{C_2O_2}$, but from the corresponding monobasic acids, viz., acetic, propionic, butyric acids, &c., by treatment with sulphuric acid. Example:—

Acetic acid.

$$HO, (C_2H_3)(C_2O_2)\,O + (S_2O_4)\,O_2 =$$

Acetic sulphuric acid.

$$2\,HO, (C_2H_2)'' \binom{C_2O_2}{S_2O_4} O_2$$

1206. The transformation noticed by Hoffmann and Buckton, which acetic acid experiences when continuously treated with sulphuric acid, *i.e.*, its change into disulphomethotic acid, consists in a simple substitution of the radical S_2O_4 for C_2O_2 in the double radical, as is expressed by the following equation:—

Acetic sulphuric acid.

$$2\,HO,(C_2H_2)'\binom{C_2O_2}{S_2O_4}O_2+(S_2O_4)O_2=$$

$$2\,HO,(C_2H_2)'\binom{S_2O_4}{S_2O_4}O_2+C_2O_4$$

In the same way, disulphetholic acid is formed from propion-sulphuric acid, thus:—

Propion-sulphuric acid.

$$2\,HO,(C_4H_4)'\binom{C_2O_2}{S_2O_4}O_2+(S_2O_4)O_2=$$

Disulphetholic acid.

$$2\,HO,(C_4H_4)'\binom{S_2O_4}{S_2O_4}O_2+C_2O_4$$

1207. From these bibasic acids may be produced, by continued treatment with sulphuric acid, new tribasic acids, if only we assume that sulphuric acid will act on propion-sulphuric acid and disulphetholic acid, as it does when propionic acid is changed into propion-sulphuric acid, thus:—

Propion-sulphuric acid.

$$2\,HO,(C_4H_4)'\binom{C_2O_2}{S_2O_4}O_2+(S_2O_4)O_2=$$

$$3\,HO,(C_4H_3)'''\left(\begin{matrix}C_2O_2\\S_2O_4\\S_2O_4\end{matrix}\right)O_3$$

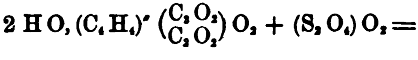
Disulphoetholic acid.

$$2\,HO,(C_4H_4)'\binom{S_2O_4}{S_2O_4}O_2+(S_2O_4)O_2=$$

$$3\,HO,(C_4H_3)'''\left(\begin{matrix}S_2O_4\\S_2O_4\\S_2O_4\end{matrix}\right)O_3$$

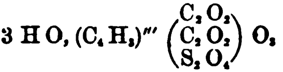
Neither of these two tribasic acids has been produced, but succinic sulphuric acid, $3\,HO, (C_4H_3)''' \left(\begin{matrix} C_2O_2 \\ C_2O_2 \\ S_2O_4 \end{matrix}\right) O_3$, is a tribasic acid of a similar composition, and its origin, from succinic acid and sulphuric acid, is quite analogous to that supposed transformation of the bibasic propionsulphuric acid into the above as yet unknown tribasic acid, as is shown by the following equation:—

Succinic acid.



$$2\,HO, (C_4H_4)' \left(\begin{matrix} C_2O_2 \\ C_2O_2 \end{matrix}\right) O_2 + (S_2O_4)\,O_2 =$$

Succinic sulphuric acid.



$$3\,HO, (C_4H_3)''' \left(\begin{matrix} C_2O_2 \\ C_2O_2 \\ S_2O_4 \end{matrix}\right) O_3$$

1208. Kolbe considers that the composition of succinic sulphuric acid affords a strong argument for the possibility suggested by him, of the existence of similarly constituted tribasic acids, which are derived from three atoms of carbonic acid, and to which belongs citric acid.

1209. The views of Kolbe on the organic compounds of nitrogen I have not given, as the views of Hofmann are already so fully given in a former part of the work. For further information about Kolbe's views the student is referred to the following papers:—

1st. Kolbe "Über de Rationelle Tusammensetzung Organischen Verbindungen."—*Annal. der Chemie*, Band, xxv.

2nd. Kolbe "Über den Naturlichen Tusammentung der Organischen mit den Inorganischen Verbindungen."—*Annal der Chemie*, Band, cxiii., 293.

APPENDIX M.

1210. In this Appendix we shall give, from Dr. Frankland's paper on organo-metallic bodies, some extracts on the formation of these bodies.

1211. Organo-metallic bodies admit of being produced by a great variety of processes; but these numerous methods of formation, with very few exceptions, admit of being grouped under four heads.

1. *Formation by union of the organic radical, in statu nascenti, with the metal.*

By this method the metal of the organo-metallic body is brought into contact with the iodide of the alcohol radical; an iodide of the metal is formed along with the organo-metallic body.

By this method the organo compounds of zinc, cadmium, magnesium, aluminum, are formed. Although the organo compounds can be formed by other processes, this is the most convenient method of producing them; and all the different series can be prepared in this way, except the two series whose general formulæ are $\mathrm{Sn}_2\left\{\begin{matrix}\mathrm{R}+\\\mathrm{R}+\\\mathrm{R}+\end{matrix}\right.$ and $\mathrm{Sn}_2\left\{\begin{matrix}\mathrm{R}+\\\mathrm{R}+\\\mathrm{R}+\\\mathrm{R}+\end{matrix}\right.$. The first of the organo compounds of mercury can be prepared by this method, but not the second series; but the members of the second series are readily obtained by the action of an organo-zinc compound upon those of the first.

2. *Formation of organo-metallic bodies by the action of the respective metals, alloyed with potassium or sodium, upon the iodides of the alcohol radicals.*

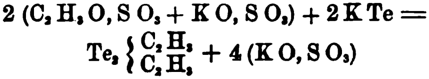
The principles involved in this second general mode of production are essentially similar to those in the first; but there is less tendency to form compounds containing negative as well as positive radicals. This method, although not capable of such general application, is more especially adapted to the formation of the organic compounds of the polyatomic metals. The simultaneous production of an organo potassium or sodium compound need not be feared, since such compounds cannot exist in the presence of the iodides of the alcohol radicals. This mode of formation we will illustrate by one example:—

$$2\left.\begin{matrix}\mathrm{C}_2\mathrm{H}_5\\\mathrm{I}\end{matrix}\right\} + \mathrm{As}\left\{\begin{matrix}\mathrm{Na}\\\mathrm{Na}\end{matrix}\right. = \mathrm{As}\left\{\begin{matrix}\mathrm{C}_2\mathrm{H}_5\\\mathrm{C}_2\mathrm{H}_5\end{matrix}\right. + 2\,\mathrm{Na\,I}$$

By this method the arsenic, antimony, tin, lead, and bismuth organo compounds can be prepared.

Organo-tellurium compounds are formed by a modification of this method, which consists in distilling telluride of potassium with sulphovinate of potash and its homologues. Example:—

Sulpho-methylate of potassium.



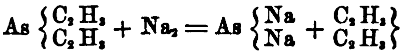
$$2\,(C_2H_3O, SO_3 + KO, SO_3) + 2\,K\,Te = Te_2\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right. + 4\,(KO, SO_3)$$

3. *Formation of organo-metallic bodies by the action of the zinc compounds of the organic radicals upon the haloid compounds, either of the metals themselves, or of their organo-derivatives.*

For the production of organo-metallic bodies containing less positive metals than zinc, this method is perhaps not only the most convenient, but also capable of the most general application. Compounds containing mercury, tin, lead, antimony, and arsenic, have been thus produced; but it has failed when applied to the haloid compounds of copper, silver, and platinum; for although these bodies are violently acted upon, the organic group does not unite with the metals.

4. *Formation of organo-metallic bodies by the displacement of a metal in an organo-metallic compound by another and more positive metal.*

Wanklyn, to whom we are indebted for this mode of formation, regards this displacement of one metal by another as a case of true electrolytic decomposition. He thinks that in zinc-ethyl, for instance, ethyl is the electro-negative, and zinc the electro-positive member. Sodium being more electro-positive than zinc, replaces the latter metal, and forms sodium-ethyl. But he supposes that when the original organo-metallic body contains a metal less electro-positive than the hydrocarbon radical, then the latter, and not the metal, would be eliminated by contact with a more positive metal. Cacodyl, for instance, when treated with sodium, should give methyl and arsenide of sodium:—



$$As\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right. + Na_2 = As\left\{\begin{matrix}Na\\Na\end{matrix}\right. + \left.\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\}$$

This view, the correctness of which is more than probable, is supported by the action of potassium and of zinc-ethyl upon ammonia:—

$$2\,N\left\{\begin{matrix}H\\H\\H\end{matrix}\right. + K_2 = 2\,N\left\{\begin{matrix}K\\H\\H\end{matrix}\right. + H_2$$

$$2\,N\left\{\begin{matrix}H\\H\\H\end{matrix}\right. + Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right. = 2\,N\left\{\begin{matrix}Zn\\H\\H\end{matrix}\right. + 2\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}$$

In accordance with this hypothesis, Wanklyn considers that the ethyl in sodium-ethyl would be displaced by copper, mercury, platinum, &c.; and that sodium-ethyl is only in equilibrium with bodies whose respective positions in the electrical scale are either both of them within, or both of them without, the space lying between the electro-positive sodium and the electro-negative ethyl.

This fourth mode of producing organo-metallic bodies has hitherto been applied only to the formation of sodium and potassium compounds, or rather double compounds of these bodies with zinc-ethyl, according to the following reactions:—

$$3\,Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right. + Na_2 = \left(2\,Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right. + Na_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.\right) + Zn_2$$

$$3\,Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right. + K_2 = \left(2\,Zn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right. + K_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.\right) + Zn$$

Sodium also displaces mercury from mercuric ethide; sodium-ethyl seems to be formed, but the exact nature of the reaction has not been ascertained.

CHAPTER XII.

ATOMIC VOLUMES OF SOLIDS AND LIQUIDS.

Introduction, 1212. *Atomic volume of solids*, 1217. *Atomic volume of liquids*, 1220.

1212. Specific gravity, or specific weight, is the comparative weight of *equal bulks* of different substances; consequently, the greater the number of atoms of a body in a given space, and the greater the weight of those atoms, the greater must be the specific gravity of the body. Now if the atomic weight of a body and the size of its atoms were known,—in other words, the number of atoms of the body which occupied a given bulk,—the specific gravity of a body could be calculated; for this weight must necessarily be the product of the atomic number and the atomic weight; since if the atoms of two or more bodies are of the same size, they will occupy equal volumes; the specific gravity of these bodies will therefore vary as their atomic weights; for examples see the 87th and following paragraphs. Atomic volumes are therefore determined, as we have seen (111) already, by dividing the atomic weights by the specific gravities. Atomic or equivalent weights give the relations by weight; atomic or equivalent volumes* give the relations by volume in which bodies unite to form chemical compounds.

1213. It will, perhaps, be more clearly seen what is understood by the numbers indicating the equivalent or atomic volumes of substances, if we represent the equivalent weights as numbers of grammes. Assuming that the equivalent of oxygen is 100, the equivalent of sulphur is 200, zinc 406, and silver 1,350. Now if we represent these numbers as so many grammes, then 406 grammes of zinc and 1,350 grammes of silver combine chemically with 200 grammes of sulphur. If we consider that all statements regarding specific weights, both of solid and fluid bodies, are calculated on the assumption that that of water is *unity*, and that 1 cubic centimeter of water weighs 1 gramme, then it follows that the specific weights of bodies express the number of grammes that 1 cubic centimeter of the body weighs. Thus the numbers 1·99 and 6·95, the specific weights of sulphur and zinc, indicate that 1 cubic centimeter of sulphur and 1 cubic centimeter of zinc weigh respectively 1·99 and 6·95 grammes. Now since the equivalent volume is obtained on dividing the equivalent or atomic weight, supposed to be expressed in grammes, by the specific gravity (the weight of one cubic centimeter expressed in grammes), it follows that the quotient, *the equivalent or atomic volume*, indicates the number of *cubic centimeters* occupied by that *number of grammes* of the body which *expresses its equivalent weight.* If we know, for example, that the equivalent or atomic weight and the equivalent or atomic volume of sulphur are respectively 200 and 100, and that for zinc they are 406 and 58, then we can readily understand that 200 grammes of sulphur occupy a space of 100 cubic centimeters, and 406 grammes of zinc a space of 58 cubic centimeters.

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* Different terms have been used to express the equivalent volumes. Kopp employs the term *specific volume*, since it is a relative number, like the specific gravity. If, instead of *equivalents*, we speak of *atoms*, the term *equivalent volume* becomes naturally converted into *atom volume*,—a term first employed by Dumas. Schröder employed, at the suggestion of Berzelius, the term *molecular volume*.

1214. As the equivalent weights and the specific gravities from which the atomic numbers are calculated are not absolute, but only relative numbers, the numbers obtained for the equivalent volumes can only be relative; therefore, when we speak of the atomic volumes of bodies, we do not mean the absolute size of the atoms, for this, like the *absolute weight* of the atoms, cannot be ascertained, but only their relative size (see par. 89). That we only obtain relative numbers as regards the atomic volumes, is at once apparent, when we consider that different numbers for the equivalent volumes are obtained, according as we employ atomic numbers on the hydrogen (= 1), or oxygen (= 100) scale; but the relation of the equivalent volumes remains still the same, whichever scale we adopt, just as the relation of the equivalent weights is unaffected by the adoption of either of the scales.

1215. As the numbers expressing the equivalent volumes are deduced from the equivalent weights and specific gravities, it is evident that the accuracy of these numbers is dependent on the accuracy with which the equivalent weights and specific gravities have been determined. Now the former are only approximations, and the specific gravities of the same substances, especially bodies in the solid state, is frequently very variable. Thus platinum, in a pulverulent state, reduced from its oxide and the double chloride of platinum and ammonium respectively, is found to have the specific gravity 17·766 in the first case, and 21·206 in the second; the numbers, therefore, expressing the atomic volumes can be, at best, but approximations; and in some cases they cannot even lay claim to this degree of accuracy.

1216. As different solid and fluid bodies have not the same degree of cohesion, and as they expand in different degrees for an equal amount of heat, it will be obvious that the difficulty of reducing the results obtained, with reference to the atomic volume of solid and fluid bodies, to general laws, will be very much greater than in the case of gases, where these disturbing causes are absent.

1217. *Atomic volume of solids.*—We have pointed out the causes which hinder our arriving at any general laws with regard to the atomic volume of solids and liquids; but although these disturbing causes affect liquid bodies, they affect solid bodies in a still greater degree, inasmuch as our knowledge of the expansion of solid bodies by heat is much more limited than that of liquids. "It is probable that the atomic volumes of solids should be compared at their melting points, since it is only at those temperatures that the effects of heat upon different solids can be said to be equal. Now the specific gravity of most solids is determined only at medium temperatures, from which the melting points of different solids are separated by intervals of very different magnitude; moreover, there are but few solids whose rate of expansion at different temperatures has been ascertained with sufficient accuracy to render it possible to calculate the specific gravities at the melting points. A further complication arises from the different densities which the same solid often exhibits, according as it is amorphous or crystalline, or according to the particular form in which it crystallizes." Metals have their specific gravities altered by hammering; their equivalent volumes are therefore altered by the same cause. Dimorphous substances, in their two forms, have different specific gravities; they have therefore two different equivalent volumes.

1218. Kopp, Schröder, and other chemical philosophers, who have devoted themselves to the consideration of atomic volumes, believe that they have discovered the laws regarding the relation of the equivalent volume of a compound to that of its constituents; but as these supposed laws do not appear to be founded on a sufficient number of well-established facts, we shall pass them over. All that is really known with respect to the relation in which equivalent volumes of compound substances stand to the equivalent volume of their constituents, may be stated in a few words:—In a few cases the equivalent volume of the compound is the sum of the equivalent volumes of its constituents; but in the majority of cases condensation occurs,—no doubt, according to certain laws, although they do not appear to be so simple as those which regulate the combination of gases.

1219. Kopp considered that the binary theory of salts was supported by the atomic volume of salts (see par. 226). He based his arguments upon the observation made by Schröder, that if from the calculated specific volume of a series of analogous combinations, such as the oxides, the volumes of the metals (the varying constituent) be deducted, the same number is often obtained to express the volume of the common constituents. Thus, on subtracting from the specific volume of the nitrates the volume of the metals entering into their composition, the number, 358, which expresses the specific volume of $N O_6$, is always obtained as the remainder. Proceeding in like manner with the carbonates, we obtain the number 151 for the volume of $C O_3$. Kopp supposed that he had deduced from these views additional arguments in support of the binary theory of salts; but if the student will refer to a memoir by Filhol, on the volumes of bodies,* he will see that these results of observation can be explained quite as well by the older view of the constitution of salts.

1220. *Atomic volume of liquids.*—We shall only lay before the student a very brief outline of the results at which Kopp has arrived in his investigations on the atomic volumes of organic liquids, as the numbers obtained can only be considered approximations, more or less remote, to the true atomic volume of liquids.

1221. As liquids expand unequally with an equal amount of heat at *equal* temperatures, it follows that their atomic volumes cannot, on account of this unequal expansion, be compared at equal temperatures; it has therefore been proposed to compare them at what are termed *corresponding* temperatures; these, if ascertainable, would be temperatures at which equal increments of heat, or more strictly of temperature, produce equal expansions. It has been conjectured, and is not improbable, that for liquids there are *corresponding* temperatures, at which the forces of their vapours are equal, viz., their respective boiling points; and according to Dalton's early discovery, temperatures equidistant from these boiling points would correspond approximately. Thus, if we wished to compare ether with alcohol,—if the boiling point of the latter body was 173° F., and its temperature was 113° below 173°, viz. 60° F., the corresponding temperature of ether, if its boiling point was 94 F., would be 113° below 94°, viz. — 19° F. The density of a liquid at its boiling point can be calculated, if its density at any one point has been ascertained, and its rate of expansion is also known.

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* "Chemical Reports and Memoirs," published by the Cavendish Society, page 63.

1222. Kopp has found that the equivalent volume of a hydrated acid* is about 537† less than that of its ether combinations. Examples:—

At. vol.
Formic ether = 1068·7
Formic acid = 522·5
Difference - 546·2

At. vol.
Acetic ether = 1345·0
Acetic acid = 797·5
Difference - 547·5

At. vol.
Butyric ether = 1865·0
Butyric acid = 1347·5
Difference - 517·5

The difference between the atomic volume of the hydrated acid and its methylic ether combination is about 252. Examples:—

At. vol.
Formiate of methyl = 782·5
Formic acid = 522·5
Difference - 260·0

At. vol.
Acetate of methyl = 1060·0
Acetic acid = 797·5
Difference - 262·5

At. vol.
Butyrate of methyl = 1581·2
Butyric acid = 1347·5
Difference - 233·7

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[*] Old view of the constitution of acids.

[†] In determining the atomic volumes of solids and liquids, it has been usual to refer their atomic weights to that of oxygen as 100.

1223. On looking at these tables, it will be seen that the difference between the atomic volume of the corresponding compounds in the ethyl and methyl series is about 253; therefore, as the two series differ by C_2H_2, it is highly probable, and it has been assumed by Kopp, that that is the atomic volume of C_2H_2 when in combination. Kopp fixes 275 as its average value at the boiling point of each compound.

1224. Isomeric liquids of analogous composition have equal atomic volumes. Examples:—

Butyric acid	$HO, C_8H_7O_3$	$= 1347{\cdot}5$
Acetic ether	$C_4H_5O, C_4H_3O_3$	$= 1345{\cdot}$
Valerate of methyl	$C_2H_3O, C_{10}H_9O_3$	$= 1865{\cdot}$
Butyric ethyl	$C_4H_5O, C_8H_7O_3$	$= 1865{\cdot}$

But if the isomeric compounds belong to different and dissimilar series, they have not equal atomic volumes. Examples:—

Acetone	$(C_6H_6O_2)_2$	$= 1932{\cdot}4$
Valerate of methyl	$C_2H_3O, C_{10}H_9O_3$	$= 1865{\cdot}0$
		$67{\cdot}4$
Aldehyd	$(C_4H_4O_2)_2$	$= 1422{\cdot}4$
Butyric acid	$HO, C_8H_7O_3$	$= 1347{\cdot}5$
		$74{\cdot}9$

It must be observed, however, that there are many groups of liquid compounds which are not isomeric which have equal or nearly equal atomic volumes.

1225. In liquids of the same chemical type, the substitution of a certain number of atoms of carbon for an equal number of atoms of hydrogen makes no alteration in the atomic volume. For example, the amyl, methyl, and ethyl compounds of valeric ($C_{10}H_{10}O_4$) and benzoic ($C_{14}H_6O_4$) acids are of equal atomic volumes. "In liquids belonging to different types, the same relations are not found to hold good. Moreover, the types within which these relations are observed are precisely those of Gerhardt's classification."—(*Watts.*)

1226. Now as the addition of C_2H_2 increases the atomic volume by 275, and since C_2 may take the place of H_2, without altering the atomic volume of the compound, it follows that the atomic volume of C_2 must be equal to that of H_2, and therefore that the atomic volume of C_2 must be one-half of 275, viz., 137·5.

1227. Oxygen, when it forms part of the radical, appears to have a different volume to what it has when it is outside the radical. In the first case, its volume appears to be rather smaller than that of hydrogen; in the latter case it appears to be rather larger.*

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* The student who desires to pursue the subject further, is referred to the papers by Otto and Filhol, in the "Chemical Memoirs" published by the Cavendish Society; also to vol. 2nd of Graham's "Chemistry," and to Playfair and Joule's memoirs on the subject, published in the "Memoirs" of the Chemical Society

CHAPTER XIII.

BOILING POINTS. FRACTIONAL DISTILLATION. SPECIFIC HEAT. ATOMIC HEAT. HEAT OF COMBINATION. CALORIFIC INTENSITY.

Introduction, 1228. *Heat and temperature*, 1230. *Thermoscopic instruments*, 1232. *Construction of the mercurial thermometer*, 1235. *Testing of a thermometer*, 1252. *Formulæ for the conversion of degrees of one scale into those of another*, 1254. *Exercises. Boiling points*, 1255. *Kopp's law of the boiling points*, 1261. *Exercises. Fractional distillation*, 1279. *Specific heat*, 1286. *Methods employed for determining the specific heat of solids and liquids*, 1290. *Measure of the sensible heat absorbed by a body*, 1291. *Exercises. Description of Regnault's method*, 1302. *Specific heat of a body not a constant quantity*, 1316. *Specific heat of gases*, 1320. *Table of specific heat of gases*, 1322. *Atomic heat of bodies*, 1323. *Relation between the specific heats and atomic weights of the elementary bodies*, 1327. *Tables of the specific and atomic heats of the elements. Atomic heats of compound bodies*, 1332. *Development of heat by chemical action*, 1335. *Description of Dr. Andrew's method*, 1343. *Combination of gaseous bodies with oxygen*, 1349. *Exercises. Combination of solid and fluid bodies with oxygen*, 1354. *Exercises. Table of the heat developed during the combination of bodies with oxygen*, 1361. *Tables of the heat developed during the combination of bodies with chlorine, bromine, and iodine*, 1368. *Influence of dimorphism on the heat evolved*, 1372. *Heat developed on the union of acids and bases*, 1373. *Table of heat evolved during metallic precipitations*, 1378. *Heat evolved on the combination of an acid with water*, 1382. *Heat evolved on the combination of a salt with water*, 1384. *Heat evolved on the combustion of polymeric compounds*, 1385. *Cold produced by chemical decomposition*, 1391. *Exceptions*, 1396. *Calorific intensity*, 1397. *Exercises. Calorific intensity of fuel*, 1404. *Exercises. Lewis Thomson's apparatus for determining the absolute heating power of fuel*, 1407. *On the burning of fuel*, 1409.

1228. What heat is, is still unknown. Two different theories have been proposed to explain its nature, but it does not come within our province to notice them.

1229. Whenever, as in the case of heat, we have to speak of any agent whose nature is unknown, the expressions and allusions we employ in regard to it must necessarily possess a degree of vagueness; and to those students who require exact definitions, they must appear unsatisfactory. This vagueness is further increased if different views have prevailed at different times as to the nature of the agent; because the terms which have been employed under one theory are frequently retained, when other and totally different views prevail. These few general observations on the terms employed we have thought it necessary to make, in order to show the student that the terms which may appear vague and unsatisfactory to him are equally so to all who study the subject.

1230. *Heat and temperature.* — The term heat we apply to the agent; the term temperature we apply to that portion of heat in a body which we can perceive by the senses. The temperature of a body can be increased or diminished. If two bodies of different temperatures are brought together, the one containing the most sensible heat—in other words, having the highest temperature—will lose heat, which the body with the lower temperature will absorb. This imparting of heat by the one body, and the receiving of it by the other, will only cease when they have both arrived at the same temperature. If, therefore, we bring the hand, or any other part of the body, in contact with a substance having a higher temperature, heat is imparted by that substance to the hand, and we experience the sensation we term heat. If, on the contrary, the hand is warmer than the substance, it imparts some of its heat to the substance, and we then experience the sensation we term cold. The student will observe, from these illustrations, that heat and cold are merely relative terms.

1231. Our sense of touch cannot be employed to ascertain the correct temperature of substances; for that will only tell us whether the substance has a higher or a lower temperature at the time, than that part of our body which comes in contact with it. The same body might even be made to feel both hot and cold *at the same moment*, if we made one hand hotter and the other colder than the body, before we brought them in contact with it. For the same reasons, we pronounce a cave hot in summer, cold in winter, although the temperature of the cave may have remained the same. To measure the correct temperature of bodies, we have recourse to the physical action of heat on bodies. These actions are of various kinds. Expansions and contractions have been adopted, as being the easiest to observe. But heat also produces electrical phenomena in bodies, on which very delicate methods of observing temperatures have been based.

1232. Instruments termed thermometers (from θερμὸς, hot, μέτρον, a measure) are employed to measure temperatures up to about 600° F. Instruments termed pyrometers (from πῦρ, fire), are employed to measure temperatures higher than 600° F.

1233. Although all bodies whatever are susceptible of dilatation and contraction, they are not equally convenient for thermoscopic agents. Mercury is the best thermoscopic agent for general purposes, as the range between its solidifying and boiling point is the widest of any liquid, and it has also the most uniform expansion. Alcohol is the only other liquid employed as a thermoscopic agent. It is employed to measure very low temperatures, as it does not solidify at the greatest known cold.

1234. We must refer the student to the general works on chemistry and physics for descriptions of the differential thermometer, the thermo-electric multiplier, the self-registering thermometer, the air thermometer, the pyrometer, —in fact, all the varieties of heat measurers but the ordinary mercurial thermometer. We shall give a brief outline of the plan of making a mercurial thermometer, in order that the student may know how it is made, —not with a view that the student should attempt to make his own thermometer, as he will be able to purchase better thermometers than any he could construct, and at a less cost. We shall also describe how a thermometer ought to be tested as to its accuracy.

1235. *Construction.*—The first essential in the manufacture of a mercurial thermometer, is a capillary tube of uniform calibre throughout its entire length, so that equal lengths of the tube will contain equal volumes of mercury. To ascertain this, a small drop of mercury is introduced into the tube, sufficient to fill rather more than a third of an inch of the tube. The mercury is gradually moved from one end of the tube to the other, and its length is measured in each successive position. The length, of course, should be the same in every part of the tube; if it be not, the tube must be rejected. Having selected the tube, the next thing to be done is to blow a bulb upon one end of it. The bulb may be either spherical or cylindrical; the last form, from exposing a large surface, is more readily affected by changes of temperature. The relative dimensions of the bore of the tube and bulb have to be taken into consideration. If the thermometer is intended to have a very open scale—in other words, to be greatly affected by comparatively small variations of temperature,—the bore of the tube must be very small, and the bulb comparatively large; but if a less degree of sensibility is required, the bore of the tube is not required so small, and the bulb is made smaller than in the first case.

1236. *Filling the thermometer.*—To facilitate the introduction of the mercury, a small funnel is frequently formed upon the other end of the tube; this is filled with mercury, the tube is slightly inclined, and the bulb is warmed by means of a spirit-lamp (see Fig. 20), in order to expand the air in the thermometer; some of the air escapes, the spirit-lamp is removed to allow the tube to cool, the air contracts, and, as a consequence, some of the mercury enters the tube. The bulb is again warmed, so as to expel a further quantity of air, the lamp is again removed, and more mercury enters from the contraction of the air; this warming and cooling the tube is continued until the bulb and part of the tube are filled with mercury. Instead of forming a funnel on the

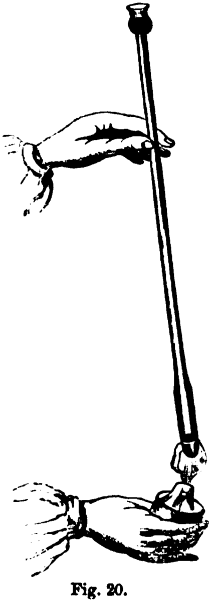

Fig. 20.

open end of the tube, and proceeding in the way we have stated, the thermometer may be filled in the following way:—The open end of the tube is plunged, after the bulb has been heated, into the mercury; on the contraction of the air some of the metal enters, the mercury in the bulb is then boiled, and the heat is continued until the tube becomes filled with mercurial vapour; the open end is then plunged again into the mercury, and as the vapour contracts the mercury enters, and so the instrument becomes filled. Whichever way the mercury has been introduced, the next thing to be determined is where, on the tube, we desire to fix some point of the thermometric scale. Suppose we desire to have the freezing point of water about 1 inch from the bulb, and the boiling point of water about the same distance from the other end of the tube, we first plunge the instrument in melting ice, and if, when it has attained the temperature of the ice, the mercury stands too high in the tube, some of the metal is expelled by heat; and if it stands too low, some more is introduced, as at the first. When the mercury stands at the proper height in the tube for the freezing point, the thermometer is introduced into boiling water, and when the mercury ceases to rise, the blowpipe flame is directed about an inch above, and the glass is then drawn out into a fine capillary. All traces of air have now to be got rid of; for this purpose the bulb is warmed until the mercury ascends through the capillary, the blowpipe flame is then directed upon the capillary, and the tube is closed and sealed. The thermometer is now tested, to see that all the air has been removed; the mode of doing this will be given when the method for testing is described. If this has been effected, the end is fashioned into a knob or ring, according as it is intended to be fixed in a wooden scale, or graduated upon the stem.

1237. *Graduation of the thermometer.*—The thermometer requires to be graduated, that is, provided with a scale to which variations of temperature can be referred; and, in order to be able to compare one thermometer with another, it is necessary, in the graduation of thermometers, to select two standard temperatures as fixed points; the temperatures, which have been universally chosen, are those of melting ice and boiling water. The thermometer ought not to be graduated immediately after it is sealed, as the bulb contracts, and does not attain its fixed dimensions until some months after the sealing; consequently, if the fixed points were determined before the bulb arrived at its fixed capacity, the graduations on the scale would indicate a temperature higher than the true one from a quarter to half a degree.

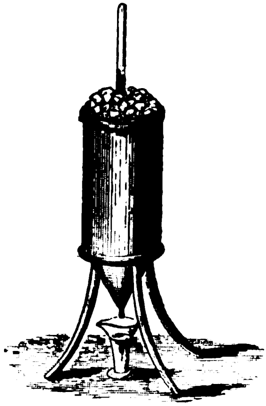
FIG. 21.

1238. We have already noticed that the melting point of ice is constant, whatever be the degree of heat, and that the temperature at which water boils in a metallic vessel at the standard pressure is also constant (49, 50, 51). The point at which the mercury stands in the tube of the thermometer at the melting point of ice is determined in the following way:—Snow or pounded ice is placed in a vessel, in the bottom of which is an aperture by which water can escape (Fig. 21). The bulb and a part of the stem of the thermometer is immersed in the ice for about a quarter of an hour, a mark is then made on the stem at the level of the mercury; this is the melting point of ice.

1239. The second fixed point, or the boiling point of water, is determined by means of the apparatus represented in the figures 22 and 23, of which fig. 23 represents a vertical section. In both, the same letters designate the same parts. The whole of the apparatus is of copper. A central tube, A, open at both ends, is fixed on a cylindrical vessel containing water; a second tube, B, concentric with the first, and surrounding it, is fixed on the same vessel, M. In this second cylinder, which is closed at both ends, there are three tubulures, *a*, E, D. A cork, in which is the thermometer, *t*, fits in *a*. To E a glass tube, containing mercury, is attached, which serves as a manometer for measuring the pressure of the vapour in the apparatus. D is an escape tube for the vapour and condensed water.

1240. The apparatus is placed on a furnace and heated to boiling; the vapour produced in M rises in the tube A, and, passing through the two tubes in the direction of the arrows, escapes by the tubulure D. The thermometer, *t*, being thus surrounded with vapour, the mercury expands, and when it has become stationary, the point at which it stops is marked. This is the point sought for. The second case, B, was added by M. Regnault to avoid the cooling of the central tubulure by its contact with the air.

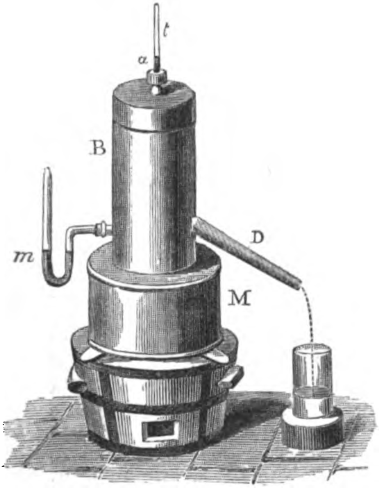

FIG. 22.

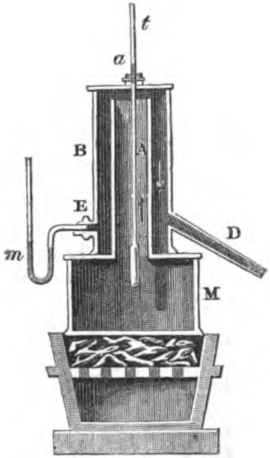

FIG. 23.

1241. The determination of the point 100° (boiling point of water) would seem to require that the height of the barometer during the experiment should be 760 mm., for when the barometric height is greater or less than this quantity, water boils either above or below 100°. But the point 100° may always be exactly obtained, by making a correction introduced by M. Biot. He found that, for every 27 mm. difference in the height of the barometer, there was a difference in the boiling point of 1°. If, for example, the height of the barometer is 778—that is, 18 mm., or two-thirds of 27, above 760—water would boil at $100\frac{2}{3}$°. Consequently, $100\frac{2}{3}$ would have to be marked at the point at which the mercury stops.*

1242. Gay Lussac observed that water boils at a somewhat higher temperature in a glass than in a metal vessel; and as the boiling point is raised by any salts which are dissolved, it has been assumed that it was necessary to use a metal vessel and distilled water on fixing the boiling point. M. Rudberg has, however, shown that these latter precautions are superfluous. The nature of the vessel, and salts in solution, influence the temperature of boiling water, but *not that of the vapour which is formed.* That is to say, that if the temperature of boiling water from any of the above causes is higher than 100°, the temperature of the vapour does not exceed 100° if the pressure is 760 mm. Consequently, the higher point may be determined in any kind of a vessel, provided the thermometer is quite surrounded by vapour, and does not dip in the water.

1243. Even with distilled water the bulb of the thermometer must not dip in the liquid; for it is only the upper layer that really has the temperature of 100°, since the temperature increases from layer to layer towards the bottom, in consequence of the increased pressure.

1244. The two fixed points having been marked on the tube, the distance between them is divided into equal parts, termed degrees. The degrees are designated by a small cipher placed a little above on the right of the number which marks the temperature; and to indicate temperatures below zero, the minus sign is placed before the figures, thus — 15° signifies 15° below zero. In accurate thermometers, the scale is marked on the glass itself, which is accomplished by covering the glass with a thin coating of beeswax, then marking the divisions and numbers with a steel point, and subsequently exposing the thermometer for a short time to the action of hydrofluoric acid gas; where the wax has been removed by the steel point the glass is etched by the gas.

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* This refers to the Centigrade thermometric scale. The difference of *one inch* of mercury in the height of the barometer raises or lowers the ebullition point by almost exactly *two degrees* of the Fahrenheit scale.

1245. There are unfortunately three different thermometric scales, viz., the Centigrade, or Celsius (the latter the name of the person who invented the scale), the Fahrenheit scale (this scale originated with an instrument maker at Dantzic), and the Réaumur scale. The Centigrade scale is adopted on the continent, especially in France, and it is the one most generally employed in scientific investigations. The Fahrenheit scale is universally employed in England for all ordinary purposes, and frequently in purely scientific investigations; it is also employed in America and Holland. The Réaumur scale is employed in Russia and Germany.

1246. The freezing point is made the zero point, both in the Centigrade and Réaumur scale; but on the Fahrenheit scale the zero point is placed at the 32nd division below the freezing point, so that on this scale the freezing point is 32°. The reason for fixing the zero of the scale at 32° below the freezing point was, that at the time it was believed to be the natural zero of temperature, or the greatest possible degree of cold. Much lower temperatures, natural and artificial, have since been observed, and it is very improbable that the absolute zero can be reached.[*]

1247. The distance between the freezing and boiling points is divided in the Centigrade scale into 100 degrees, so that 0° C. represents the one point, and 100° C. the other; the distance between the two points on the Réaumur scale is divided into 80 degrees, so that 0° R. represents the one point, and 80° R. the other. The distance between the two fixed points is divided on the

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[*] "Reckoning from 0° C. upwards, we find that every degree added to the temperature of a gas produces an augmentation of elastic force equal to $\frac{1}{273}$ of that which the gas possesses at 0°, and, hence, that by imparting 273° we double the elastic force. Supposing the same law to hold good when we reckon from 0° *downwards*—that for every degree of temperature *withdrawn* from the gas we diminish its elastic force, or the motion which produces it, by $\frac{1}{273}$ of what it possesses at 0°, it is manifest that at a temperature of 273° C. below 0°, we should cease to have any elastic force whatever. The motion to which the elastic force is due must then vanish, and we reach what is called the *absolute zero of temperature*.

"No doubt, practically, any gas deviates from the above law of contraction before it sinks so low, and it would become solid before reaching —273° C., or the absolute zero. This is considerably below any temperature which we have as yet been able to obtain."—"*Heat considered as a Mode of Motion,*" *by Tyndal.*

Fahrenheit scale into 180 degrees, so that 32° F. represents the *one*, and 212° F. the other point. The length of a degree having been thus ascertained by dividing the distance between the two points, the tube is graduated in degrees of the same length below the freezing point, and above the boiling point, as far as may be desired.

1248. "A scale divided upon the principles already described evidently depends for accuracy on the supposition that equal increments of heat produce an equal amount of expansion. With due precautions, a pound of water at 32° F. mixed with a pound of water at 212° F. should yield a mixture in which the thermometer should stand at 122°, the exact mean. Yet it is not true that even in the same substance equal increments of heat, at *different* temperatures, produce an equal amount of expansion: for example, the expansion of mercury for the 10 degrees between 30° and 40° is less than its expansion for the 10 degrees between 200° and 210°. In the mercurial thermometer, for temperatures between freezing and boiling water, it may nevertheless be assumed, without sensible error, that equal increments of heat raise the thermometer through an equal number of degrees. The increase in the capacity of the glass bulb, especially if the thermometer be made of crown glass, almost exactly compensates for the increasing rate of the expansion of mercury; though for temperatures above this point the compensation is not so exact. The general result is, that for all bodies, in proportion as the temperature rises the expansion increases; the distance between the particles augments with the heat, and consequently their mutual cohesion is more readily overcome. The total expansion of mercury, for example, for three progressive intervals of 180° F., according to Regnault, is the following:—between 32° and 212° it is 1 part in 55·08; between 212° and 392° it is 1 in 54·61; and between 392° and 572°, 1 in 54·01.

1249. "The temperature of 572° F. as measured by an air thermometer, if measured by the expansion of mercury in an ordinary thermometer, would be indicated as 586°, because the apparent dilatation of the mercury increases as the temperature rises." *

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* Miller's "Elements of Chemistry," vol. i.

1250. The mercurial thermometer cannot be employed for temperatures below —33° F., as mercury solidifies at —40° F.; and it cannot be employed with accuracy for temperatures above 580° F.

1251. "The whole thermometric scale is to be regarded as purely arbitrary, and may be compared to a chain, extending indefinitely both upwards and downwards. We select some point on the chain, and begin to count the degrees from that. We fix the length of our degrees by selecting a second point, at a convenient distance above the first, and dividing the intervening length into an arbitrary number of equal parts. Thus, all is arbitrary; and there is no peculiar virtue in the two points which have been chosen, other than that they can be easily determined with accuracy, and include between them the range of temperature with which we are usually most concerned."

1252. *Testing of a thermometer.*—When a thermometer is introduced into melting ice, the level of the mercury in the tube should stand exactly at the point of the scale which indicates this temperature; and when it is suspended in the steam of boiling water, the level of the mercury should stand, at the standard pressure, exactly at the point of the scale which indicates the temperature of boiling water. To ascertain whether the value of the degrees is uniform throughout the entire length of the tube, a little column of mercury must be detached from the rest of the metal, the tube must then be inclined so as to make the small column pass from one part of the tube to another part, and we must ascertain by measurement whether it occupies the same length in the tube in each position. To ascertain whether the air has been perfectly expelled before sealing the tube, the instrument must be inverted, so that the bulb is uppermost; if the mercury descends with ease *quite* to the end of the tube, we may be satisfied that the air is absent in that part of the instrument. But there may be some in the bulb—to ascertain this, we must observe whether the bubble which is in the bulb during the time it is inverted entirely disappears when we restore the instrument to its proper position; if it does, the thermometer is perfect as regards the entire absence of air.

1253. "Sometimes a thermometer, when inverted, does not allow the mercury to descend, and inexperienced persons are liable to imagine that air must necessarily be present; but the effect alluded to is frequently caused by the adhesion between the mercury and the glass; if, however, we warm the bulb, so as to cause the mercury to ascend in the tube, and then invert the instrument, the metal should descend; and if no moderate tapping or swinging will make it do so, we may safely conclude that air forms the impediment."*

1254. As it is frequently necessary to translate the figures on the Celsius scale into those of Fahrenheit, and *vice versâ*, we have given a table at the end of the book, by which the degrees on the one scale can be converted into those of the other at a glance. But it is necessary to know how to convert the one into the other by calculation, which is easily accomplished; 100° C. = 180° F., or 5° C. = 9° F.;† hence, $1° F. = \frac{9}{5}° C. + 32$: the 32 is added because the zero of Fahrenheit is 32 Fahrenheit degrees below the *zero* of the Centigrade. The conversion is easily effected by the use of the following formulæ:—

Fahrenheit to Centigrade	-	$\frac{5}{9}(F.° - 32) = C.°$
Centigrade to Fahrenheit	-	$\frac{9}{5}\ C.° + 32 = F.°$
Réaumur to Fahrenheit	-	$\frac{9}{4}\ R.° + 32 = F.°$
Fahrenheit to Réaumur	-	$\frac{4}{9}(F.° - 32) = R.°$

EXERCISE.

190. Reduce 60° F. to the degrees of C. and R.; 60° of R. to F.°; 50° C. to F.°; 20° F. to C.°; —2·2° F. to C.°; —2° C. to F.°; —5·8° F. to C.°; 5° C. to F.°; —24° *C. to* F.°; —36° C. to F.°.

1255. *Boiling points.*—We have already noticed (50) that the temperature at which each liquid boils is quite constant under the same circumstances. We have also seen (1242) that other circumstances besides pressure influence the temperature at which liquids boil; but these circumstances do not affect the temperature of the vapour of the boiling liquid; this at once adjusts itself to the pressure of the atmosphere, and is always constant for the same liquid under the same pressure. In determining, therefore, the boiling point of a liquid we do not allow the bulb of the thermometer to dip into the liquid, but we bring it almost into immediate contact, so that it may be completely surrounded by the vapour.

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* "Hand-book of Chemical Manipulation," by Greville Williams.

† Measuring on both scales from the freezing to the boiling point, the interval between these two points is divided into 100° on the Centigrade, and 180° on the Fahrenheit scale.

1256. As the boiling point of any body of definite composition, and perfectly pure, is stationary during the entire time it is kept boiling, whilst the boiling point of a mixture of substances keeps constantly increasing as the more volatile substances evaporate, the boiling point becomes the most important physical character for determining the identity and purity of a volatile liquid.

1257. The size of the glass vessel in which the liquid is to be boiled will depend upon the quantity of liquid at our command. If we have only a small quantity, we may employ a test tube fitted with a cork; the cork must be pierced with two holes, in one of which is inserted the thermometer, and in the other the exit tube. If we have a large quantity of liquid at our command, we may employ a tubulated retort; the tubulure is fitted with a cork pierced with one hole, in which the thermometer is inserted. If we do not wish to lose any of the liquid, we condense the vapour by connecting the exit tube from the test tube, or the beak of the retort, with a Liebig's condenser. The liquid is boiled until the greater part of it has distilled over: we note the pressure of the barometer, and we also note the temperature during the whole time.

1258. The temperature indicated by the thermometer is less than that of the true boiling point, if only part of the stem of the thermometer is exposed to the vapour of the liquid. For a thermometer to indicate the true temperature of vapour or any other medium, it is necessary to immerse both the bulb and stem in the medium whose temperature is to be measured; for if the stem of the thermometer is exposed to a lower temperature than the bulb, the whole of the mercury will not be fully expanded, and the thermometer will indicate too low a temperature: this difference between the indicated and the true temperature becomes important when the temperature of the medium greatly exceeds that of the air.

1259. As it is impossible, in testing the temperature of a small quantity of liquid, to immerse the thermometer completely, it is necessary in all exact researches to add to the observed temperature a small correction. For making this correction, it is necessary to know the mean temperature of the exterior portion of the column of mercury exposed to the air, compared with that part below the cork, surrounded by the vapour; for this purpose we fix to the stem of the first a second thermometer, in such a way that its reservoir is about the middle of the column of mercury which is above the distillatory apparatus.

If we represent by T° the temperature indicated by the thermometer in the vapour, by t° the mean temperature, and by N° the number of degrees which the exterior mercury column measures; lastly, by δ, the co-efficient of the apparent expansion of mercury in glass ($\delta = 0{\cdot}000154$ for 1° C.), the quantity to be added to T° for obtaining the true boiling point becomes,—

$$N.\,(T - t)\,\delta.$$

As an example, suppose we have found $171{\cdot}3^\circ$ C. $= T$ for the boiling point of the liquid, with a thermometer having 25 degrees above zero in the distillatory apparatus; in this case, $171{\cdot}3^\circ - 25$, or $146{\cdot}3^\circ = N$. If the exterior thermometer indicates $43^\circ = t$ for the mean temperature of this portion of the column of mercury, $171{\cdot}3^\circ - 43^\circ$, or $128{\cdot}3^\circ = (T - t)$. The correction becomes then,—

$$146{\cdot}3^\circ \times 128{\cdot}3 \times 0{\cdot}000154 = 2{\cdot}9^\circ,$$

and we find that the true boiling point of the liquid under the observed barometric pressure is

$$171{\cdot}3^\circ + 2{\cdot}9^\circ = 174{\cdot}2^\circ.$$

1260. Organic compounds are more volatile in proportion as they contain a greater number of atoms of hydrogen, and a smaller number of atoms of carbon, oxygen, and nitrogen. Of polymeric compounds, the one whose compound atom contains the smallest number of elementary atoms is always the most volatile.

1261. *Kopp's law of the boiling points.*—Kopp pointed out some years ago (1841), *that in analogous compounds the same difference of composition frequently involves the same difference in boiling points.* The assertion of the existence of this law-like relation between the chemical composition of substances and one of their most important physical properties, when first enunciated was objected to by many chemists. The objections led Kopp to collect additional evidence in favour of his views, and to show more particularly that in very extensive series of compounds (alcohols, $C_n H_{n+2} O_2$; acids, $C_n H_n O_4$; compound ethers, $C_n H_n O_4$, &c.), an elementary difference, $x\ C_2 H_2$, is attended by a difference of $x \times 19°$ in the boiling points, and how this fact is intimately connected with other regularities exhibited by the boiling points of organic compounds.

1262. Although the existence of the relations between chemical composition and boiling point is *now* generally acknowledged, and in many cases the recognition of these relations has furnished important arguments in discussions regarding the true molecular value of organic compounds; nevertheless, Kopp is of opinion that these relations have scarcely been sufficiently appreciated, as important means of control in experimental inquiries, and the aid which they are frequently capable of lending in the determination of the true chemical character of a new compound.

1263. In a memoir in the *Philosophical Transactions* for 1860, Kopp points out the facts and principles which have been established, and which he thus sums up:—"It is especially with regard to organic compounds that constant relations between boiling point and composition have been demonstrated. It often occurs that in the case of analogous compounds the same difference in the boiling points corresponds to the same difference in the chemical formulæ, or that the differences in boiling points and those in composition are proportional. In different series of analogous compounds the same differences of boiling-point may correspond to the same differences of composition, but this does not obtain in all series. The regularities exhibited by the boiling points of organic compounds, and more especially the observation of the same difference of boiling point corresponding to the same difference of composition, are limited to certain groups. In other groups, the same difference in the formulæ involves another difference in the boiling points." *

1264. We have already noticed (1261) that among the earliest recognised regularities, comprising at the same time the largest number of compounds, are the following:—

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* In Kopp's paper the old atomic weights for carbon and oxygen are employed, and the Centigrade scale.

1st. An alcohol, $C_n H_{n+2} O_2$, which contains $x C_2 H_2$ more or less than another, boils at a temperature $x \times 19°$ higher or lower.

2nd. An acid, $C_n H_n O_4$, boils at a temperature 40° higher than the alcohol, $C_n H_{n+2} O_2$, the oxidation of which alcohol may give rise to the acid.

3rd. A compound ether, $C_n H_n O_4$, boils at a temperature 82° lower than the acid, $C_n H_n O_4$, isomeric with it.

1265. If we start from the boiling point of ethyl-alcohol, which is 78°, these three propositions enable us to calculate the boiling points of all the alcohols, acids, and compound ethers represented by the above general formulæ.

1266. The boiling points of the series of alcohols, acids, and compound ethers which we have just considered, are closely connected with those of other monatomic alcohols with two equivalents of oxygen, represented by the general formulæ, $C_n H_m O_2$; of other monobasic acids with four equivalents of oxygen, represented by the general formulæ $C_n H_m O_4$; and of the ethers generated by these acids and alcohols, the general formulæ of these ethers being $C_n H_m O_4$. It is frequently observed that a compound of this series, which, when compared with an analogous body in the first series, contains $x \times C$ of more or less, but which contains the same number of oxygen and hydrogen equivalents, boils at a temperature $x \times 14{\cdot}5°$ higher or lower, or (what amounts to the same thing) that it boils at a temperature $x \times 5°$ lower or higher, accordingly as it contains $x \times H$ more or less.

EXAMPLES.

1. Benzoic acid, $C_{14} H_6 O_4$, for example, contains 8 of C more than the acid $C_6 H_6 O_4$. the boiling point of which is 137°; consequently, the boiling point of benzoic acid will be $137 + 8 \times 14{\cdot}5 = 253$. It contains 8 H less than the acid, $C_{14} H_{14} O_4$, the boiling-point of which is 213°. Comparing it, therefore, with this standard ($C_{14} H_{14} O_4$), its boiling-point, by calculation, will be $213 + 8 \times 5 = 253$.

2. Allyl-alcohol, $C_6 H_6 O_2$. contains 2 C more than ethyl-alcohol, $C_4 H_6 O_2$, which boils at 78°; the calculated

boiling point of allyl-alcohol, accordingly, is 78 + 2 × 14·5 = 107; or it may be compared to the alcohol $C_6H_8O_2$, the boiling point of which is 97°, when the boiling point of allyl-alcohol, which contains 2 H less, will be found by calculation = 107 (= 97 + 2 × 5).

1267. In all the series of analogous combinations which have been considered, a compound containing in its formula $x\,C_2H_2$ more than another, is found to boil at a temperature $x \times 19°$ higher. The same regularity obtains in other series of analogous compounds, but by no means in all.

1268. We also find, on comparing the boiling points of the corresponding terms in the several series of homologous substances hitherto considered, that many other constant differences in boiling point correspond to certain differences in composition. Thus, a monobasic acid is found to boil 44° higher than its ethyl compound, and 63° higher than its methyl compound; and this constant relation holds good even for acids other than those we have previously noticed. The substitution products of acetic acid afford suitable examples of this. The boiling point of monochloracetic acid (185°—188°) has been found to be about 44° higher than that of the monochloracetate of ethyl (143·5°). Starting from the boiling point of trichloracetate of methyl (145°), or from that of trichloracetate of ethyl (164°), the boiling point of trichloracetic acid is found by calculation to be 208°. Dumas found it, by experiment, to be about 200°.

1269. In a few substances other than acids, the substitution of C_4H_4 for H is occasionally attended by a decrease of 44° in the boiling point; that of C_2H_2 for H by a decrease of 63°.

1270. Not in all homologous series does the elementary difference, $x\,C_2H_2$, involve a difference of $x \times 19°$ in boiling point. Kopp shows that this difference is greater for the hydrocarbons, C_nH_{n-6}, and C_nH_{n+2}; for the acetones and aldehydes, $C_nH_nO_2$; for the so-called simple and mixed ethers, $C_nH_{n+2}O_2$; for the chlorides, bromides, and iodides of the alcohol radicals, C_nH_{n+1}, and for several other groups. That it is, on the contrary, smaller for the anhydrides of monobasic acids, $C_nH_{n-2}O_6$; for the ethers, $C_nH_{n-2}O_8$ (which may be formed either by the action of one molecule of a dibasic acid, $C_n H_{n-2} O_8$ upon two molecules of a monatomic alcohol, $C_n H_{n+2} O_2$, or by the action of two molecules of a monobasic acid, $C_n H_n O_4$, upon one molecule of a diatomic alcohol, $C_n H_{n+2} O_4$, and several other series.

1271. Kopp thinks "that there can be no doubt that in different series of homologous compounds the difference of boiling point corresponding to the elementary difference $x\, C_2 H_2$ may vary; that frequently it is found to be $x \times 19°$, but sometimes more, sometimes less. *As to* these inequalities of differences, they are sure to be governed by a more general law, which will probably be recognised when a sufficient number of boiling-points shall have been determined under a pressure different from the ordinary pressure of the atmosphere; for it cannot, by any means, be taken for granted that two substances will exhibit the same difference of boiling point, whatever may be the pressure. Let S and S_1 be the boiling points of two liquids under the ordinary pressure, and s and s_1 the boiling points under another pressure; then the assumption of $S - S_1 = s - s_1$ would involve the inference $S - s = S_1 - s_1$; that is, that the boiling points must go under precisely the same change for the same change of pressure. But this conclusion—the so-called law of Dalton—*is by no* means correct; and it may be legitimately held, that the homologous substances which under the ordinary pressure do not exhibit the most frequently observed difference of boiling point (19°), for the elementary difference, $C_2 H_2$, would certainly show that difference under a different pressure. But sufficient data are still wanting for the appreciation of the mode in which differences in boiling points are affected by changes of pressure.

1272. Isomeric compounds belonging to the same type, and possessing the same chemical character, have the same boiling point.

1273. Isomeric compounds belonging to the same type, but possessing a different chemical character, have different boiling points.

1274. Isomeric compounds belonging to different types have different boiling points.

1275. The determination of the boiling point of a compound, together with an examination of the substances with which the compound is serially allied in boiling point, may be of great assistance in fixing its character, the type to which it belongs, and the series of homologous bodies of which it is a term. Example:—The boiling point of the so-called eugenic acid (251°) shows that this substance, although represented by the formula $C_{20}H_{12}O_4$, cannot possibly be homologous to benzoic acid, $C_{14}H_6O_4$ (boiling point observed, 250°; calculated, 253°). This result might be inferred with the greatest probability from the boiling point of the two substances, even if cuminic acid, isomeric with eugenic acid, and the homologue of benzoic acid, were not known. On the other hand, when the boiling points of eugenic acid and of hydride of salicyl, $C_{14}H_6O_4$ (boiling point, 196°) are considered, it becomes extremely probable that these two bodies are homologous. (To the difference in composition, $C_6H_6 = 3\,C_2H_2$, corresponds in this case the difference in boiling points, $250 - 196 = 54 = 3 \times 18°$.)

1276. The boiling points of polymeric compounds are also different, and may serve to determine the formula representing a substance.

1277. Kopp calls attention to the boiling points of the organic bases, but I must refer the student to Kopp's Memoir for his views on the boiling points of these bodies, merely remarking that I do not think we have yet sufficient data for drawing any general conclusions respecting the composition and series to which these bodies belong from this physical character.

1278. The comprehensive recognition of definite relations between composition and boiling point is, for the present, chiefly limited to organic compounds. But for the majority of these compounds, and indeed for the most important ones, this relation assumes the form of a simple law, which, more especially for the monatomic alcohols, $C_nH_mO_2$; for the monobasic acids, $C_nH_mO_4$; and for the compound ethers generated by the union of the two previous classes, is proved in the most general manner; so much so, indeed, that in many cases the determination of the boiling point furnishes most material assistance in fixing the true position and character of a compound. And it deserves more especially to be noticed, that the simplest and most comprehensive relations have been recognised for those classes of organic compounds which have been longest known and most accurately investigated; and that even for those classes the generality and simplicity of the relation, on account of numerous boiling points incorrectly observed at an earlier date, appeared in the commencement doubtful, and could be more fully acknowledged only after a considerable number of new determinations. Thus we are justified in hoping that in other classes also of compounds, in which simple and comprehensive relations have not hitherto been traced, these relations will become perceptible as soon as the verification of the boiling points of terms already known, and the examination of new terms, shall have laid a broader foundation for our conclusions.

EXERCISE.

191. Calculate the boiling points of the following substances:— Methyl-alcohol, ethyl-alcohol, amyl-alcohol, cetyl-alcohol, formic acid, acetic acid, proprionic acid, caprylic acid, formiate of methyl, acetate of methyl, formiate of ethyl, acetate of ethyl, formiate of butyl, valerate of ethyl, butyrate of propyl, acetate of amyl, allyl-alcohol, phenyl-alcohol, angelic acid, benzoic acid, valerate of allyl, benzoate of allyl, cinnamate of methyl.

1279. *Fractional distillation.*—When several volatile substances, of different boiling points, occur mixed together, distillation is frequently employed in such cases as the *separating* process, just as crystallization is employed to separate crystalline bodies, or fractional precipitation to separate solid bodies. The distillation is conducted in the following manner:—The mixture is introduced into a retort, which the student will see, as we proceed with the description, must be a large one. A thermometer is placed in the tubulure of the retort, as described in par. 1257. The boiling point of the substance, as it is a mixture, will not be stationary, but will keep gradually ascending (1256). To effect the separation of the substances, the receiver must be changed at every 10° F. or 5° C. Each of the fractions thus obtained must be submitted to a second fractionation, and each fraction obtained in the second fractionation must be submitted to a third, and we must continue to repeat the fractionations *until each fraction has a constant or almost a constant boiling point.* The different substances composing the original mixture are then perfectly separated, or at least as perfectly as this process can make them.

1280. We will treat the subject under the following heads:—1st. That the process is one of great labour, if the mixture is a complex one. 2nd. Modifications of the process in special cases. 3rd. The process not an accurate one in all cases. 4th. Examples of the separation of bodies by this process.

1st. If the mixture begins with a low boiling-point, and rises very high, the great labour required in such an investigation will be apparent, when we consider the number of fractions which will be obtained, even in the first distillation, and that each fraction, when submitted to the second fractionation, will probably be divided into four or five fractions. Thus, for instance, if the mixture commenced to boil at 200° F. and rose to 400° F., twenty fractions would be obtained in the first fractionation; and if the liquids were fractionated fifteen times, as was the case in the investigation of naphtha from Boghead coal, by Greville Williams, and in the investigation of the bases from Dippel's oil, by Dr. Anderson, 300 distillations would be required *at least;* but in each of the investigations we have named, 1,000 distillations were made.

We may here observe, that the boiling points of the fractions are lower in the second than in the first distillation, and this depression of the boiling point continues sometimes to take place up to the sixth fractionation, and the superior limit of temperature of the first distillation is extended in the second, &c. Example:—Mansfield, in his examination of light coal naphtha, observed a great depression in the point at which ebullition commenced in the case of each successive fraction in the second distillation; while, on the other hand, the thermometer index rose far higher than the superior limit of temperature, below which the same fluid was distilled in the first fractionation. For instance, the fraction which commenced from the boiling point, 230° F. in the first distillation, began to boil at about 196° F. in the second; while of the same portion, all of which was received below 239° F. in the first, more than a quarter remained unvolatilized at 248° F. in the second distillation, so that each fraction of 9° F. in the first was distributed over from 54° to 72° F. in the second fractionation. This lowering of the boiling points is not due, in the majority of cases, to a decomposition of the substances, but to a gradually increasing separation of the less volatile portions of the mixture.

The student will see, from what has already been stated, that though a large retort will be required for distilling the original mixture, if complex, much smaller retorts will be required for distilling the fractions.

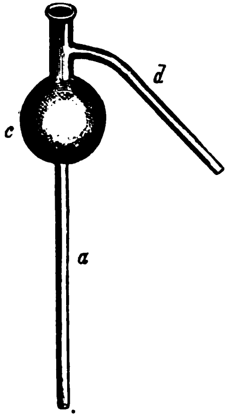

Fig. 24.

2nd. If it is intended merely to isolate a more volatile fluid from a less volatile one, Wurtz' apparatus (Fig. 24) may be employed with great advantage. The tube, *a*, is fixed by means of a perforated cork in the neck of the flask in which the liquid is to be distilled. The thermometer is fixed by means of a perforated cork in the opening, *b*, the bulb of the thermometer resting in the bulb, *c*. The tube, *d*, forms the exit tube. The portion of the vapour of the less volatile fluid which is carried upward by the vapour of the more volatile one, is condensed in the bulb, *c*, and flows back into the flask, whilst the vapour of the more volatile one passes on through the exit tube, *d*, and thus the two fluids become separated. Max Dürre found this apparatus very useful in the fractional distillation of the light coal naphtha obtained from the destructive distillation of brown coal.

Wurtz' apparatus is very similar in principle to the one which Mansfield contrived for the separation, on the large scale, of benzole from toluole, cumole, cymole, and other hydrocarbons in coal-tar. Mansfield's apparatus is shown in fig. 25. A is the retort, or boiler, which is charged with the coal naphtha, from which the vapours, as they are evolved, are conducted into B, the head, through the neck, C. D is a pipe which leads from the top of B to any convenient condenser, represented in the diagram by a still-worm, E; from the mouth of which, F, the benzole

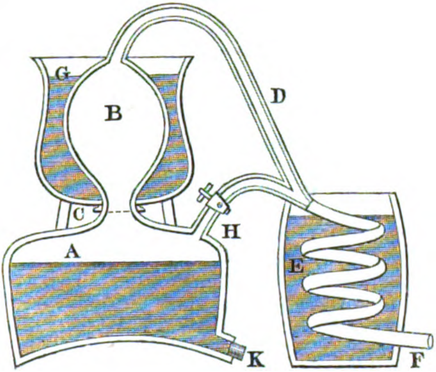

FIG. 25.

runs. B is enclosed, below and on the sides, in an outer vessel, G, which is open above, and nearly filled with water, which need not be changed during the operation. H is a secondary neck, through which the remainder of the naphtha, after the extrication of the benzole, may be distilled off, by turning on the tap, I. K is a pipe for running off the tarry residue.

As there is a wide interval between the boiling point of benzole and the boiling points of the other hydrocarbons we have named, the separation of the benzole from these other hydrocarbons becomes, on account of this difference, comparatively easy. When heat is applied to the retort, A, the temperature of the naphtha in A will gradually rise, until at last it boils; the vaporized portion, when it comes in contact with the cold inner surface of B, will be condensed, and flow back into A; B, and the water in G, become warmed by this condensation; the temperature of the water soon reaches nearly to the boiling point of benzole, which will therefore distil over rapidly, while so much of the toluole, and oils having higher boiling points, as is carried up into B with the benzole vapour, is still almost entirely condensed, and returned into the retort. The benzole continues to distil till the naphtha is exhausted of it, and the temperature of the water goes on rising until it boils; no liquid then remains in the retort that has not a boiling point at least 25° F. above that of water.

Sometimes it is necessary, in the separation of volatile substances, to make the liquid boil at a lower temperature than it does at the ordinary pressure of the atmosphere; the boiling point may be lowered by distilling in an atmosphere of a gas which is lighter than that of atmospheric air; but the most effectual plan is to reduce the pressure of the atmosphere by connecting the apparatus with an air-pump.

When the difference in the boiling points of the liquids which have to be separated is less than from 40° to 50° C., it is difficult, if not impossible, to separate them by distillation under the ordinary conditions: we are sometimes able to effect a separation in such cases, in distilling under a reduced pressure, because the difference in the tension of their vapours is frequently greater under the diminished pressure. This process is applicable, for example, to a mixture of alcohol and ether; less of the alcohol distils over when the mixture is distilled at a low temperature. These results are obtained if we effect the distillation in an apparatus in which a vacuum has been made, after the retort and the receiver have been placed in cooling mixtures of different temperatures, the receiver being placed in the one of the lowest temperature. We can place the retort, A (fig. 26), in ice, and the receiver, B, in a mixture of ice and crystallized chloride of calcium; the cork *a*, which attaches the retort and receiver, is covered with sealing-

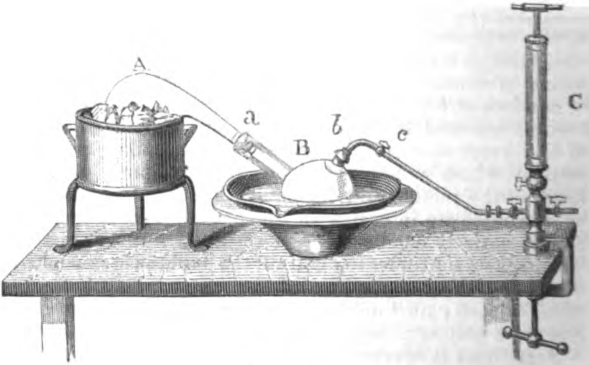

FIG. 26.

wax; also the cork *b*, which connects the receiver with the tube of lead: the other end of the lead tube is connected with an air-pump, C; the lead tube is provided with a stopcock, *c*. When the vacuum has been produced, ebullition commences; the stopcock, *c*, is then shut; the distillation continues, on account of the difference in temperature which exists between the receiver and the retort: for arresting the distillation the stopcock is opened, and air allowed to enter.

When the organic substances are oxidized by the air at the temperature at which they boil, they are distilled in a current of dry hydrogen or carbonic acid; to effect this, we fix in the tubulure of the retort a tube communicating with the apparatus in which the gas is disengaged, and it dips down to the bottom of the liquid to be distilled: before commencing this distillation, the entire apparatus is filled with the gas; the current of gas is continued during the whole time the distillation is carried on.

Instead of distilling alterable liquids in an atmosphere of an inert gas, we may distil them in a current of steam; the vapours of many oils have, for example, a tension sufficiently great, at the temperature of 100° C., for being carried over by the aqueous vapour, and condensed with it. Many of the essences to which plants owe their perfume can be isolated by this means.

When the liquid is a mixture of two bodies, we can sometimes succeed in separating them by heating the liquid with a chemical reagent which attacks one of the bodies without altering the other. This process can be applied to a great number of essential oils; these liquids are generally a mixture of a substance composed of carbon and hydrogen (frequently in the proportion of essence of turpentine), and of another substance, composed of carbon, hydrogen, and oxygen; caustic potash generally attacks the latter substance, whilst it is without action upon the former. In cases of this kind, we can either effect the separation by treating the essential oil with a concentrated solution of potash, which will dissolve the oxygen compound, or by distilling the essential oil off solid caustic potash, which will unite with the oxygen compound, and thus prevent it from distilling over with the other substance.

3rd. Even when a constant boiling point has been obtained, the liquid, if the original mixture was a complex one, may still be a mixture of different families of hydrocarbons (see pars. 1283 and 1284). Greville Williams, who has had great experience in fractional distillations, observes,—"This process (fractional distillation) is not only one of great labour, but, unfortunately, it has little claim to accuracy as regards the *absolute* separation of bodies, it being, perhaps, almost impossible to procure one substance out of a mixture of homologous fluids in such a state that it can be said to contain no admixture of its associated compounds.* This arises from the fact that the boiling point of an organic fluid is dependent upon the relative number of atoms of carbon and hydrogen present, the former element raising, while the latter lowers the degree at which it is converted into vapour (1260); it will therefore be seen, that on endeavouring to separate bodies by this means, when homologous groups are present, it is possible to obtain fluids having the theoretical boiling point, and proportion of carbon and hydrogen in the hundred parts, and yet being admixtures of the fluids above and below in the homologous series, the deficiency in the carbon and hydrogen of those lower in the series being exactly counterbalanced by the excess in that portion present belonging to a higher position in the group. This mode of separating bodies is always, therefore, to be considered as by no means preventing the necessity for further modes of purification being adopted in all possible cases, and it is only with some neutral hydrocarbons that any great difficulty occurs in this respect."

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* Dr. Wanklyn has quite recently communicated a paper on this subject to the Royal Society, of which the following is an abstract:—When we mix liquids of different boiling-points together, and distil the mixture, it does not by any means follow that the liquid of *lowest* boiling point will distil over the *fastest*. The liquid of lower boiling point will give off the greater *volume* of vapour, but the liquid of higher boiling point not unfrequently gives off the *greater weight* of vapour. In estimating whether of two liquids will boil off faster when they are mixed, it is not only necessary to take into account the *tension* of the vapours at the boiling point of the mixture, but also the *specific gravity* of the vapours. Dr. Wanklyn gives the following example:—He took equal weights of methyl-alcohol and iodide of ethyl, and distilled the mixture; he found that iodide of ethyl, although it has a higher boiling point than methyl-alcohol, distils over much faster than that liquid. He applies the principle to explain why homologues are so difficult to separate. The higher the formula of a homologue the higher is its boiling point, but, what tends to neutralise this, the higher is the specific gravity of the vapour which it gives off. He also explains, on the same principle, why oils distil over so readily with watery vapour. Oily vapours are heavy, watery vapour is light; a small *volume* of oily vapour represents therefore comparatively a great weight.

4th. We will now give a brief outline of the actual processes which were followed in the separation of the volatile bases from bone oil, and the separation of the hydrocarbons in coal naphtha:—

1281. Dr. Anderson commenced the isolation of the different bases in bone oil in the following way: he first redistilled the bone oil of commerce, and when about two-fifths of the oil had passed over, a point was attained at which the temperature required to be raised considerably; the receiver was changed for the purpose of collecting the less volatile portion apart; the distillation was then continued until the bottom of the retort reached a red heat. Organic bases were found to be present in both distillates, and as they were thus crudely separated into two classes, the first distillate containing the more volatile, and the second distillate the less volatile ones, the distillates were separately treated for the removal of the bases from the oils: the treatment was the same in each case.

1282. The distillate was treated with sulphuric acid diluted with about ten times its weight of water; the fluids were left in contact for a week or two, during which time they were frequently agitated; after the lapse of that time the acid solution was drawn off, and the oil continued to be treated with fresh quantities of acid, until all the bases were removed: the different acid solutions were mixed together. Dr. Anderson added to the acid mixture thus obtained more acid, and then introduced the mixture into a retort and distilled, as he thought it possible that some of the more volatile bases might escape from the acid on the application of heat; they would thus have been lost if the solution was evaporated in an open vessel; but this was not found to be the case, as only some non-basic oil and water distilled over: in the latter liquid Runge's pyrrol[*] was found to be present. As no bases were found to escape from the acid, the solution was transferred from the retort into an evaporating dish, and evaporated to a small bulk. After the evaporation the liquid was strained through calico to remove the tar which had separated during the evaporation; it was then introduced into a retort, and lime,* potash, or soda (each of these bases answers equally well) was added in excess; the solution was then distilled, care being taken to condense all the bases. Stick potash was added to the distillate in order to separate the bases from the water; on the addition of the potash the bases floated on the top, and were then removed and subjected to fractional distillation, the receiver being changed at every 10° F., the different fractions re-fractionated, and this was continued until constant boiling points were obtained. The different bases thus isolated were submitted to the usual examination of basic bodies, to determine their composition, atomic weight, &c.

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[*] Volatile organic bases with very high boiling points are decomposed during distillation with the formation of pyrrol ($C_4 H_5 N$); this body is recognised by its characteristic reaction of staining fir-wood, moistened with hydrochloric acid, bright red or crimson. In the formula given for pyrrol $C = 12$.

1283. Greville Williams found, in his investigation of the volatile bases produced by the destructive distillation of bituminous shale, that, even after constant boiling points had been obtained, the bases were not completely separated; he has therefore proposed, in the place of fractional distillation, the fractional crystallization of the platinum salts of the bases.†

1284. To determine the nature and composition of the different hydrocarbons which may be present in such substances as coal-naphtha, or the so-called mineral oils of America and Canada, the naphtha is first treated with dilute sulphuric acid (one part of acid to about nine of water), so as to remove any organic bases which may be present. After the removal of the acid mixture the naphtha is washed with water, and then treated with a dilute solution of potash, to remove any organic acids which might be present. After the removal of the alkaline liquid, the naphtha is washed several times with water; and in order that the bases may be completely removed, the treatment with the acid and with the alkali is repeated. The naphtha is now submitted to fractional distillation, the receiver being changed at every 10° F., and the fractionation is repeated until each fraction has a constant, or almost constant boiling point. Greville Williams found, in his investigation of the naphtha from Boghead coal, that even after the fractions had attained a constant boiling point, three series of hydrocarbons were present, viz., the alcohol radicals, the benzole series, and the olefiant gas series; he ascertained the presence of these bodies, and separated them in the following manner:—

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* The only objection to the employment of lime is the large quantity of insoluble sulphate of lime which is formed, and which settles down on the bottom of the retort.

† "The difficulties in the way of separating several basic liquids of analogous constitution by fractional distillation are so great, that it would appear quite hopeless to obtain any one product absolutely pure, even when the quantity of material at command is very considerable; but by first fractionating the liquid by distillation, and then converting the fractions into platinum salts, and repeatedly crystallizing, until the product gives exactly the theoretical quantity of platinum, we may, by distillation with potash, obtain the base in a state fit for the examination of its properties."—Greville Williams "On Pyridine among the Volatile Bases in the Naphtha from the Bituminous Shale of Dorsetshire, and on the Fractional Crystallization of Platinum Salts:" *Philosophical Magazine*, 1854.

1st. Each fraction is treated in a flask with a mixture of nitric acid and sulphuric acid: after the addition of the acid the mixture is repeatedly shaken; the acid is then removed, and the hydrocarbon liquid is continued to be treated with concentrated nitric acid, until, on the addition of water to the acid liquid, no further separation of nitro-compounds occurs; the acids remove the members of the benzole and olefiant gas series. The liquid unacted upon by the acid is then washed with water, dried by being digested on stick potash, and when dry is distilled several times over sodium. The analysis of these bodies gave the carbon and hydrogen in the proportion of the alcohol radicals, and also of the hydrides of the alcohol radicals; thus the fraction distilling between 115° and 121° F. gave the formula $C_8 H_{18}$; this corresponds to the alcohol radical butyl, but it also corresponds to the hydride of the radical of caprylic alcohol. Williams concluded from the boiling points and the vapour densities, that these bodies were alcohol radicals, and not the hydrides of these radicals. He has submitted these bodies to a fresh investigation, to determine whether they are alcohol radicals or their hydrides; he now concludes they belong to the latter class of bodies, as we shall immediately see.

2nd. Another portion of the different fractions was taken for determining what members of the olefiant gas and benzole series were present; to effect their separation, each fraction was cohobated with about half its bulk of fuming hydriodic acid in a flask for about three or four hours. The neck of the flask was then cut off, and replaced by a bent tube connected with a condensing apparatus. On applying a gentle heat the hydrocarbons unacted on slowly distilled away. The more volatile portion having in this manner been removed, the distillation was carried on in a current of steam until the distillate began to sink in water. The receiver was then changed, and the product collected apart. The hydriodic acid converts the olefiant series into the iodides of the monatomic radicals, whilst the other two series of hydrocarbons are unacted upon, and are distilled off.

3rd. The benzole series were removed by treating the mixture with fuming nitric acid (475).

1285. Greville Williams has once more endeavoured to determine whether the bodies unacted upon by nitric acid in the coal naphtha are the alcohol radicals, or the hydrides of these radicals. As he was not aware of any reactions which distinguish the two classes of bodies, he attempted the solution in the following manner:—ethyl and hydride of amyl are isomeric bodies; the first is a gas and the latter is a liquid at common temperatures; therefore, if a *liquid* having this composition could be discovered in the naphtha, it must be hydride of amyl, and not ethyl. The search was made, and a liquid, having the composition of, and also agreeing in vapour density with hydride of amyl, was discovered; he concludes from this result, that the indifferent hydrocarbons are, in all probability, homologues of marsh gas, and only isomeric with the true alcohol radicals. Since then, Schorlemmer has commenced the investigation of the naphtha produced in the destructive distillation of cannel coal; he separated the indifferent hydrocarbons from the olefiant and benzole series in the way Williams had done, viz., by nitric acid. He concludes that these hydrocarbons are the hydrides of the alcohol radicals, and not the radicals themselves, because they are transformed by the action of chlorine into their corresponding chlorides. He found in the oil boiling below 120° C. the following four hydrides:—

$C_{10}H_{12}$	hydride of amyl -	boiling	point	39° C.
$C_{12}H_{14}$	hydride of hexyl -	„	„	68° C.
$C_{14}H_{16}$	hydride of heptyl -	„	„	98° C.
$C_{16}H_{18}$	hydride of octyl -	„	„	119° C.

He also found these four hydrides in the oils known by the name of the turpentine substitute, and obtained as the first product in the rectification of the crude American rock oil. He found that different samples of these oils, as found in commerce, possess very different properties; the specific gravity lies between 0·70°—0·75°. One sample began to boil at 30° C., and the greatest portion distilled over below 100° C., whilst the boiling point of other samples ranged between 80°—150° C., and others between 100°—200° C.

1286. *Specific heat.*—If equal quantities of the *same* liquid, at *different* temperatures, are mixed together, the temperature of the mixture will be the *mean* of the two; thus, if one pound of water at 60° is mixed with the same quantity at 212°, the temperature of the mixed mass will be 136°. But if equal weights of *different* fluids are mixed together, the temperature of the mixture will not be the *mean* of the two; thus, if one pound of mercury at 40° is mixed with the same quantity of water at 156°, the temperature of the mixture will be 152·3°. Therefore, whilst the temperature of the water has only been depressed 3·7°, enough heat has been evolved to raise the temperature of the mercury 112·3°. If we substitute volumes for weights, we find that water requires double the quantity of heat that an equal volume of mercury requires, to raise it a certain number of degrees; thus, if two glass vessels, one containing water and the other an *equal volume* of mercury, be immersed at the same time in a hot water bath, it will be found that the mercury becomes heated to the temperature of the water in the bath, in *half the time* that the water in the glass vessel requires to gain that temperature; and if the vessels containing the mercury and water be removed from the bath, after the two liquids have arrived at the same temperature, the mercury, it will be found, will cool *twice as rapidly* as the water. To take another example; if one pound of iron filings at 68° be placed in one pound of water at 32°, the temperature of the mixture will be 36°; consequently, the quantity of heat, the loss of which lowers the temperature of the iron 32°, increases the temperature of the water only 4°. It is evident from these examples, that equal weights and equal volumes of *different* substances require the addition of different quantities of heat to produce the same alteration in their temperature; hence, different bodies at the same temperature, and whose volumes or weights are equal, contain *unequal* quantities of heat.

1287. From what has just been stated, the student will see clearly that the thermometer only measures the temperature of bodies, and not the amount of heat they contain; for different bodies, at the same temperature, and whose volumes or weights are equal, contain unequal quantities of heat. Unequal quantities, by volume or weight, of the *same* body, may also indicate the same temperature, though the larger quantity must necessarily contain more heat than the lesser quantity; for instance, the water in a wineglass will have the same temperature as the water in a cistern, if filled from the same source. "In one condition only the thermometer becomes a direct measure of the amount of heat; and that is in the case of the same weight of the same substance. Thus, if we take the 1 lb. of water, it is true that, if a given amount of heat will raise its temperature one degree, twice the amount of heat will raise its temperature two degrees; here, then, we have a unit for measuring the amounts of heat."

1288. The *absolute quantity* of heat which a body gains or loses cannot be measured; but we can ascertain how much one body gains or loses compared with another, either by the process of mixing described in the examples we have given, or by other methods which we shall presently describe; we ascertain by these methods the relative quantities of heat which equal bulks or weights of different substances require, to raise them to a given temperature. Thus we have already noticed, that if one pound of mercury at 40° is mixed with one pound of water at 156°, the mixed mass will have a temperature of 152·3°. Consequently, the same weight of water requires, according to these numbers, rather more than thirty times as much heat as mercury requires to produce the same elevation of temperature; as mercury requires a less amount of heat than water to raise it a given number of degrees, it is said to have a *less capacity for heat* than water. The capacities for heat of all solid and liquid bodies are expressed in numbers in relation to that of water; these numbers are termed the specific heats of bodies.

1289. The unit chosen for comparison, and called the *unit of heat*, or the *thermal unit*, is not everywhere the same. In France it is the quantity of heat necessary to raise the temperature of *one* kilogramme of water, or one gramme, from 0° to 1° C. The English unit of heat is the quantity of heat required to raise one pound of water one Fahrenheit degree between 55° and 60°. Others adopt as the thermal unit the quantity of heat necessary to raise one pound of water from 0° to 1° C. When water is taken as the standard for the comparison of specific heats, we mean by the term the specific heat or calorific capacity of a body, the quantity of heat which is required to raise the body through a given range of temperature, from 0° to 1° C., for example, compared with the quantity of heat which the same weight of water would require, to be raised through the same range of temperature. Thus, if we take five vessels, containing respectively one pound of water, one pound of sulphur, one pound of iron, one pound of silver, one pound of mercury, and expose them all to such a source of heat that equal amounts must enter each vessel during the same time,—if, now, we observe the thermometers which have been placed in these vessels, we shall find, when the temperature of the water has risen one degree, and consequently, when one unit of heat has entered each vessel, that the temperatures of the other substances have increased by the number of degrees given in the second column of the following table. By the principle just established, it follows that, if one unit of heat will raise the temperature of one pound of mercury 30°, it will only require one-thirtieth as much, or 0·033 of a unit of heat, to raise the temperature of the same weight one degree. In like manner, the fractional parts of a unit of heat required to raise the temperatures of one pound of each of the other substances one degree can be easily calculated, and are given in the third column of the table; these fractional parts are termed the specific heats of the substances:—

	Temperature.	Unit of heat (Specific heat).
Water	1·0°	1·000
Sulphur	4·9	0·203
Iron	8·8	0·114
Silver	17·5	0·057
Mercury	30·0	0·033

Water, then, at the same temperature, contains 4·9 times as much heat as the same weight of sulphur, 8·8 times as much as the same weight of iron, 17·5 times as much as the same weight of silver, and 30 times as much as the same weight of mercury; and, in like manner, we should find that at the same temperature, and for equal weights, water contains more heat than any solid or liquid known. Hence the specific heat of solid or liquid substances is always expressed by fractions.

1290. "Three methods have been employed for determining the specific heat of solids and liquids,—the method of the melting of ice, the method of mixtures, and that of cooling. In the latter, the specific heat of a body is determined by the time it takes to cool, through a certain temperature. Before describing these methods, it is important to explain how we measure the quantity of heat absorbed by a body of which the mass and the specific heat are given, when the temperature is elevated a certain number of degrees.

1291. *Measure of the sensible heat absorbed by a body.*—"Let m be the weight of a body in pounds, c its specific heat, and t its temperature. The quantity of heat necessary to raise one pound of water from 0° to 1° C. being taken as unity, it will require m of these units to raise m pounds of water from 0° to 1° C.; and to raise this last weight (m pounds) from zero to t degrees, it will require t times as much, that is to say, $m\,t$. Now, since this is the quantity of heat necessary for raising from zero to t degrees m pounds of water, whose specific heat is 1, it is evident that, for a body of the same weight, whose specific heat is c, it will require c times $m\,t$, or $m\,t\,c$; consequently, when a body is heated through t degrees, the quantity of heat which it absorbs is *the product of its weight into its temperature into its specific heat.* This principle is the basis of all the formulæ for calculating specific heats.

1292. "If a body is heated or cooled from t to t' degrees, the heat absorbed or disengaged will be represented by the formula—

$$m\,(t' - t)\,c, \text{ or } m\,(t - t')\,c.$$

1293. "A thorough comprehension of these formulæ will prevent any difficulty in the solution of problems on specific heat."—(*Ganot.*)

1294. *Method of the fusion of ice.*—Black employed a block of ice in which a cavity was formed, and which was provided with a cover of ice, as a *calorimeter*. The substance whose specific heat had to be determined was heated to a certain temperature, and then placed in the cavity, and covered with the ice cover. When the body had become cooled to zero, the cavity was opened, and both the substance and the cavity wiped perfectly dry with a cloth which had been previously weighed. The cloth was subsequently weighed; the increase in weight gave, of course, the quantity of ice which had been converted into water; and from the weight of ice *melted* was calculated the specific heat of the body. Lavoiser and Laplace substituted a more complicated apparatus for the block of ice employed by Black, on account of the difficulty of obtaining ice in sufficiently large blocks. This apparatus is termed the ice calorimeter; but as the results which are obtained by it are inaccurate, on account of the difficulties which attend its use, we shall not describe it further.

1295. *Method of mixtures.*—The specific heat of a body is determined by this method in the following way:—The body is weighed, and then raised to a known temperature, by keeping it, for instance, in a current of steam for some time; it is then immersed in *cold water*, the *weight* and *temperature* of which are known. The amount of heat communicated to the water will be proportional to the specific heat of the substance examined, and gives us the data for calculating it.

1296. "Let M be the weight of the body, T its temperature, and c its specific heat; and let m be the weight of the cold water, and t its temperature.

1297. "As soon as the heated body is plunged into the water, the temperature of the latter rises until both are at the same temperature. Let this temperature be θ. The heated body has been cooled by $T-\theta$; it has, therefore, lost a quantity of heat, $M(T-\theta)c$. The cooling water has, on the contrary, absorbed a quantity of heat equal to $m(\theta-t)$; for the specific heat of water is unity. Now the quantity of heat given up by the body is manifestly equal to the quantity of heat absorbed by the water; that is, $M(T-\theta)c = m(\theta-t)$, from which—

$$c = \frac{m(\theta-t)}{M(T-\theta)}$$

1298. "An example will illustrate the application of this formula:—A piece of iron weighing 60 ounces, and at a temperature of 100° C., is immersed in 180 ounces of water, whose temperature is 19° C.: after the temperatures have become uniform, that of the cooling water is found to be 22° C. What is the specific heat of the iron?

1299. "Here the weight of the heated body, M, is 60; the temperature, T, is 100°; c is to be determined; the temperature of mixture, θ, is 22°; the weight of the cooling water is 180, and its temperature 19°; therefore—

$$c = \frac{180\,(22 - 19)}{60\,(100 - 22)} = \frac{9}{78} = 0{\cdot}1153."$$

EXERCISES.

192. Taking the specific heat of iron as 0·115, how much sensible heat would be absorbed by 10 lbs. of iron raised from 0° to 20° C.?

193. How much heat would be disengaged if 15 lbs. of copper were cooled down from 100° to 5° C., its specific heat being 0·096?

194. If 3 lbs. of mercury, at 30° C., are mixed with 3 lbs. of water, at 10° C., and the temperature of the mixture is found to be 10·639° C., what is the specific heat of the mercury?

195. If 0·685 lb. of sulphur, at 60° C., is immersed in 4·573 lbs. of water, at 12° C., and the temperature of the mixture is 13·42°, what is the specific heat of the sulphur?

1300. It is obvious that the vessel which holds the cooling water must change its temperature with that of the water, so that the heat lost by the substance which is cooled not only raises the temperature of the water, but also the temperature of the material of which the vessel is composed, to the same degree. In accurate experiments, the amount of heat required for this purpose must be estimated and allowed for. The amount is easily estimated, if we know the weight of the vessel, and the specific heat of the substance of which it is made. The vessel is usually a small cylinder of silver or brass, with thin, polished sides, so that these data can be readily obtained. "If the weight of the vessel be m', and its specific heat c', its temperature, like that of the water, is t; consequently the previous equation becomes—

$$Mc\,(T - \theta) = m\,(\theta - t) + m'\,c'\,(\theta - t)$$

from which, by obvious transformations,—

$$c = \frac{(m + m'\,c')\,(\theta - t)}{M\,(T - \theta)}$$

Generally speaking, the value, $m'\,c'$, is put $= \mu$; that is to say, μ is the weight of water which would absorb the same quantity of heat as the vessel. This is said to be the *reduced value* in water of the vessel. The expression accordingly becomes—

$$c = \frac{(m + \mu)\,(\theta - t)}{M\,(T - \theta)}."*$$

1301. In accurate experiments, it is necessary also to allow for the heat absorbed by the glass and mercury of the thermometer; and if, as is usually the case, the substance is enclosed in a glass tube in a small basket of wire-work, it is also necessary to pay regard to the weight and specific heat of these envelopes in the calculation. This method of determining the specific heat of solids and liquids admits of great accuracy, but its practical application requires many precautions, owing to the numerous sources of error.

EXERCISES.

196. A piece of iron weighing 20 grammes at the temperature of 98° C. is dropped into a glass vessel weighing 12 grammes, and containing 150 grammes of water at 10° C. The temperature of the water is thus raised 10·29° C. Required the specific heat of the iron, knowing that the specific heat of the glass is 0·19768.

197. Calculate the specific heat of oil of turpentine from the following data:—42·57 grammes of the oil at 33·7 were mixed with 470·3 grammes of water at 12·23°. The temperature of the mixture was found to be 15·57°;

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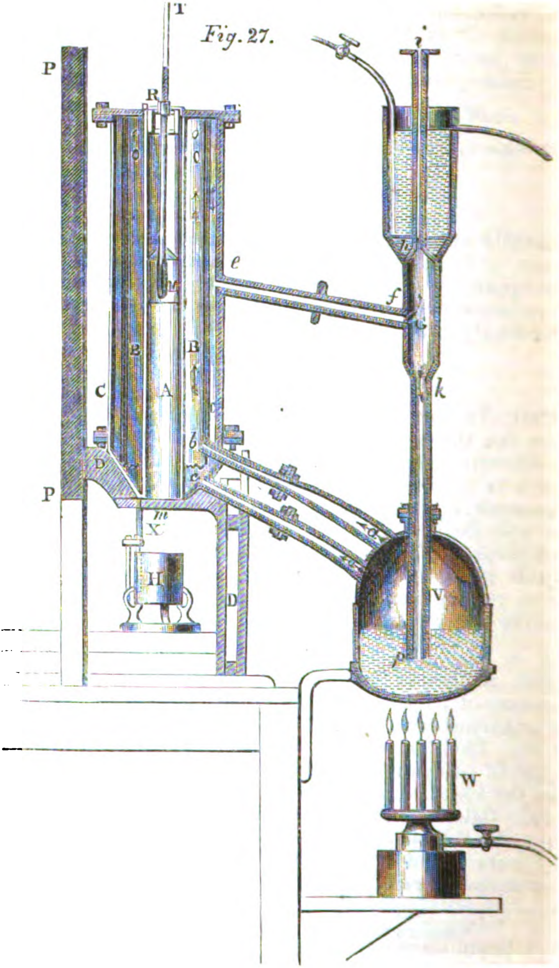
* Ganot's "Physics." Edited by Dr. Atkinson.

Fig. 27.



the water was contained in a copper vessel weighing 45·25 grammes, and having a specific heat equal to 0·035.

1302. Regnault adopted this method in his very extended investigations on the specific heat of bodies. We shall give his own description of the last form of apparatus (Fig. 27) he employed. In the Memoir* in which he describes the apparatus, he states that he brings together the experiments he has made during several years for determining the specific heat of some simple bodies which he had never before succeeded in obtaining in sufficient quantity, and of a sufficient degree of purity. The methods which he employed for this new series of experiments differ little from those which he employed in his former experiments. He replaced the charcoal stove, which he employed in his former researches, by a gas lamp. This he found to be a great advantage.

1303. The substance submitted to examination is placed, generally, in a small basket of brass wire, M, provided in the interior with a cylinder of brass, in which is placed the bulb of the thermometer, T, which gives the temperature of the basket and its contents. The basket is suspended by a silk thread, which traverses the hollow metallic stopper, R. The thermometer, T, is maintained by this same stopper in such a manner that the division corresponding to 100° does not differ from the heat of the stove by a centimetre.

1304. The heated stove or steam bath is formed of three concentric cylinders of tin plate. The interior cylinder A, in which is placed the basket and thermometer, is hermetically sealed at the top and the bottom to the exterior envelope. Its superior orifice is formed by the hollow stopper R; its inferior orifice is closed by a moveable damper *m*, by which we heat the basket with the substance which it contains. Between the outer cylinder and the cylinder A is placed an intermediate one, which is fixed to the superior cover, and descends to the bottom of the conical part of the outer cylinder. The stove is maintained by a wooden support, DDPP′, which serves besides as a screen for preventing the heat radiating upon the calorimeter H, where it occupies the place indicated in the figure, at the moment when we wish to immerse the heated basket.

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* "Sur la Chaleur Spécifique de quelques Corps Simples." Par M. V. Regnault.—*Annal de Chimie et de Physique*, 1861.

1305. The boiler V communicates with the stove by the tube *a b*, which traverses the intermediate envelope, and brings in the vapour by the annular space B B, round the interior cylinder A. This vapour escapes by the openings *oo*, opening upon the opposite side to that by which the tube *a b* enters: the vapour re-descends through the exterior annular space C C; the condensed water returns to the boiler V, by the lower tube *c d*. The vapour which has preserved the gaseous state escapes from the stove by the pipe *ef*, and is conveyed into the larger pipe G, terminating in the top by a narrower pipe, which is surrounded by cold water, which is being continually renewed. The vapour is completely condensed by this refrigerator, and returns to the boiler by the tube *k p*; moreover, it returns with a temperature very near 100° C., because in the space G it traverses the vapour which constantly arrives from the stove.

1306. The boiling of the water in the boiler V is produced by the gas lamp W; it continues to burn as long as is desired without requiring any attention; the same quantity of water serves indefinitely, as it returns without loss to the boiler.

1307. This new arrangement of the apparatus renders the operation extremely simple, and permits the experimenter to be occupied with other work.

1308. If we replace the water in the boiler V by other volatile liquids, we can obtain in the stove stationary temperatures very different from 100° C. Thus, if we employ, in the place of the water, sulphide of carbon, the temperature will be 46° C.; if we employ chloroform, the temperature will be 60°; with alcohol the temperature will be 78° C.; with turpentine the temperature will be 157° C.; &c. It is very easy to obtain in the stove a stationary temperature perfectly fixed; it suffices to place in the boiler V a liquid, the boiling point of which, under the ordinary pressure of the atmosphere, is little different from that which we wish to obtain in the stove; and then make this liquid boil under a greater or less pressure than the atmosphere, so that the thermometer of the stove is rigorously fixed at the temperature we wish to obtain. In this case we make the tube *h i* communicate, by an intermediate tube of lead, with a reservoir of air, the pressure of which can be changed at will by an exhausting or forcing pump.

1309. When we wish to determine the specific heat of a liquid, or of a body which liquefies at a temperature little higher than that of the surrounding air, we are obliged to have recourse to the inverse method, which consists in cooling the body in a freezing mixture, and determining the depression of temperature which is produced by its immersion in the calorimeter. Regnault has replaced the instrument which he employed in his earlier experiments by another which is more easily managed, and which permits of the better regulation of the temperature. The cold is produced by the vaporization of a very volatile liquid in a continuous current of air, and which can be regulated at pleasure. Fig. 28 represents a vertical section of the apparatus. A central tube A, similar to that in Fig. 27, and provided at its two extremities with the same connections, receives the basket M, containing the substance whose specific heat has to be determined. It is enclosed in another tube, B, having the form shown in the figure, and which is hermetically sealed to tube A at the top and bottom. A

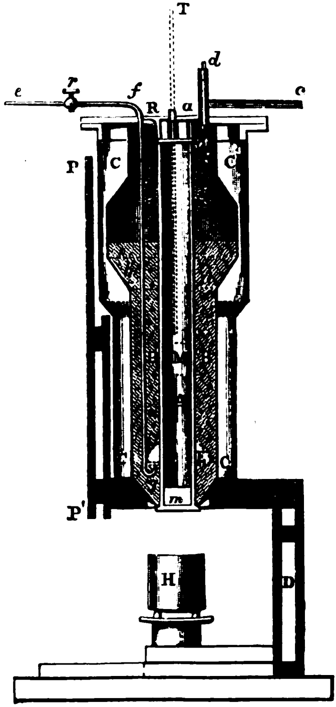


FIG. 28.

third tube, C, encloses the other two; it preserves the tube from contact with the surrounding air, and thus prevents the dew from being deposited upon it.

1310. On the top of the tube B are two tubulures: to one is soldered the three-branched tube *b a d c*; the second is traversed by a bent tube, *e f g*, provided with a stop-cock, *r*, and which descends to the bottom of the tube B. Lastly, the whole of the apparatus is placed upon a support provided with a screen, similar to that employed for Fig. 27.

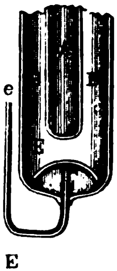
1311. The volatile liquid, ether or sulphide of carbon, is poured into the tube B, by the orifice *d*, which is afterwards closed. In order that the level of the liquid be not lowered below *h i*, by reason of its evaporation during a prolonged experiment, the tube B is enlarged towards the top.

1312. A current of air is forced in by the tube *e f g*, either by the aid of an aspirator adapted to the tubulure *c*, or by a forcing-pump which is attached to the tube *e f g*. Large reservoirs, into which air was forced by means of the pump until it had a pressure of several atmospheres, were employed by Regnault; one of these reservoirs, charged with compressed air, was connected with the tube *e f g*. In opening more or less the stop-cock *r*, a current of air, more or less rapid, traverses the ether in the tube B, and escapes saturated with vapour by the tubulure *a c*. The temperature is rapidly lowered by reason of the evaporation. When the ether approaches the lowest temperature which is desired—and this is made known by the thermometer which is plunged in the ether—the opening of the stop-cock is contracted so as to arrest the cooling, and after a little practice the operator is able to render the temperature stationary for as long a time as he desires. The thermometer T, the bulb of which is plunged into the basket M, is necessarily slower than that in the ether, but the two thermometers indicate the same temperature after the current of air has been regulated. The basket M is not lowered into the calorimeter until the equilibrium is nearly established.

1313. We cannot obtain with this apparatus as low a temperature as we can with ice and crystallized chloride of calcium. Thus, when the external temperature is + 20° C., it is difficult to maintain the ether at a stationary temperature below — 12°C. With sulphide of carbon, under the same circumstances, the temperature descends only to — 8° C. But the facility of maintaining these low temperatures stationary for a long time renders these results more accurate.

1314. Another arrangement permits the gradual lowering of the temperature of a liquid, and of rendering it stationary at the degree which we wish. Regnault has frequently employed it for determining the temperature at which a liquid solidified, when the solidification ranged between — 15° C. and + 10° C. The interior tube, A, is then closed at the bottom. In it is placed the liquid, and a thermometer, which gives the temperature, and also serves as a stirrer. By the aid of a current of air, we depress continuously, and also as slowly as we wish, the temperature of the ether; the thermometer plunged in the liquid equally lowers up to the moment solidification commences; its temperature then becomes stationary. To find the melting-point, we diminish the current of air, or arrest it completely: the temperature of the ether then rises. We agitate continually the liquid with the thermometer, and we observe if, at the moment it begins to ascend, the solidified substance has entirely returned to the liquid state.

Fig.29



1315. Lastly, if it be desired, for special experiments, to obtain a temperature below — 40° C., liquid ammonia is employed in the place of ether. The current of air traverses the liquid ammonia with a sufficient swiftness to lower the temperature even to — 80° C. In regulating the current, we can render the temperature stationary at any degree between — 40° and — 80°. The great latent heat of vaporized ammonia renders this regulation very easy.

1316. The specific heat of a body is not a constant quantity, it increases with the temperature; a greater amount of heat is therefore required to raise a body one degree at a high, than at a low temperature. Examples:— The specific heat of water at 180° C. is 1·0364; the mean specific heat of silver, between 0° and 100°, is 0·0557; while between 0° and 200° it is 0·0611. The student will now understand the reason why, in the definition of the unit of heat, a particular temperature, and not 1° at any temperature, was named.

1317. The specific heat of a body is greater in the liquid than in the solid state: thus the specific heat of water is 1, that of ice is 0·504; liquid bromine, 0·111, solid bromine, 0·081; melted tin, ·0637, solid tin, ·05623. Knowing these facts, we might infer what is really the case,—that the increase of specific heat with the temperature is greatest as solid bodies approach the melting point; and that the specific heat of solids diminishes with the increase in their density, or molecular aggregation. Examples:—Solid copper, when annealed, has a specific heat equal to ·09501; but by hammering its density is increased, and consequently its specific heat is diminished. The specific heat of copper which has been hammered is ·0936. The density of tin and lead is not increased by mechanical pressure; their specific heats are not, therefore, diminished by pressure. The specific heat of a substance is not the same in its different allotropic modifications; in these cases, also, the specific heat diminishes as the density of the substance increases. Example:—

	Specific gravity.	Specific heat.
Wood charcoal	0·300	0·2415
Graphite	2·300	0·2027
Diamond	3·500	0·1469

1318. The specific heat of liquids, with the exception of water, increases with the temperature much more rapidly than that of solids.

1319. Mercury, on account of its small specific heat, is rapidly heated and cooled. This property, as well as some of its other properties, renders it well adapted for a thermometric agent. Water, on the other hand, from its great specific heat, requires a long time in being heated or cooled. For the same weight and temperature, it absorbs or gives out far more heat than any other known liquid or solid, and is only exceeded by that of hydrogen. The ocean becomes, from this property of water, the great storehouse of heat; and we can at once see the important part water plays as the great regulator of climates, on account of this property. Comparing equal weights, the specific heat of water being 1, that of atmospheric air is 0·25; hence 1 lb. of water, in losing 1° of heat, would raise the temperature of 1 lb. of air 4°, or 4 lbs. of air 1°; but, owing to its much less density, 1 lb. of air fills about 770 times the space of 1 lb. of water; consequently, 4 lbs. of air fill 3,080 times the space; therefore, water, by parting with 1° of heat to the air, increases with that heat the temperature of 3,080 times its own bulk of air 1°. A large quantity of heat becomes stored up in the ocean in summer, which is slowly restored to the air in winter. "Hence one cause of the absence of extremes in an island climate. In various parts of the Continent fruits grow which our summers cannot ripen; but in these same parts our evergreens are unknown; for they cannot live through the winters. The winter of Iceland is, as a general rule, milder than that of Lombardy."

1320. *Specific heat of gases.*—The specific heat of gases is referred either to that of water or air. The specific heat of a gas does not vary with the temperature, and Regnault has found that it does not vary with the pressure, and hence is the same for all densities.

1321. "From the calculations of Laplace and Poisson, and the experiments of Clement and Desormes, of De la Roche and Berard, and of Gay Lussac and Dulong, it has hitherto been assumed that the specific heat of a gas under a constant pressure is always greater than the specific heat under a constant volume; but M. Regnault has lately found, by an entirely new method, that the difference between the two kinds of specific heat is either null or extremely small."

1322. Further on we give the specific heats of most of the elementary bodies: in the following table we give Regnault's determinations of the specific heats of a considerable number of gases and vapours. In the column headed "By weight," is meant the number of heat units required to raise the temperature of equal weights (water = 1) from 0° to 1° C., assuming that the gas is allowed to expand freely, and that the pressure is constant.

Specific heat of gases and vapours.

Name of gas or vapour.	Specific heat.		Specific gravity.
	By weight.	By volume.	
Simple gases.			
Air	0·2377	0·2377	1·000
Oxygen	0·2182	0·2412	1·1056
Nitrogen	0·2440	0·2370	0·9713
Hydrogen	3·4046	0·2356	0·0692
Chlorine	0·1214	0·2962	2·4400
Bromine	0·0552	0·2992	5·3900
Compound gases.			
Protoxide of nitrogen	0·2238	0·3413	1·5250
Deutoxide of nitrogen	0·2315	0·2406	1·0390
Carbonic oxide	0·2479	0·2399	0·9674
Carbonic acid	0·2164	0·3308	1·5290
Sulphide of carbon	0·1575	0·4146	2·6325
Sulphurous acid	0·1553	0·3489	2·2470
Hydrochloric acid	0·1845	0·2302	1·2474
Sulphide of hydrogen	0·2423	0·2886	1·1912
Ammonia (gas)	0·5080	0·2994	0·5894
Marsh gas	0·5929	0·3277	0·5527
Olefiant gas	0·3694	0·3572	0·9672
Vapours.			
Water	0·4750	0·2950	0·6210
Alcohol	0·4513	0·7171	1·5890
Ether	0·4810	1·2296	2·5563
Cyanide of ethyl	0·4255	0·8293	1·9021
Chloride of ethyl	0·2737	0·6117	2·2350
Bromide of ethyl	0·1816	0·6777	3·7316
Sulphide of ethyl	0·4005	1·2568	3·1380
Acetic Ether	0·4008	1·2184	3·0400
Chloroform	0·1568	0·8310	5·3000
Dutch liquid	0·2293	0·7911	3·4500
Acetone	0·4125	0·8341	2·0220
Benzole	0·3745	1·0114	2·6943

Name of gas or vapour.	Specific heat.		Specific gravity.
	By weight.	By volume.	
Vapours—continued.			
Oil of turpentine	0·5061	2·3776	4·6978
Terchloride of phosphorus	0·1346	0·6386	4·7445
Terchloride of arsenic	0·1122	0·7013	6·2510
Chloride of silicon	0·1329	0·7788	5·8600
Bichloride of tin	0·0939	0·8639	9·2000
Bichloride of titanium	0·1263	0·8634	6·8360

1323. *Atomic heat of bodies.*—If, in place of determining how much heat is required to raise *equal weights* of the elements, we determine how much is required to raise *the atomic weights* of these bodies *through an equal number of degrees*, we find that all the elementary bodies yield one of two numbers: these numbers are in the proportion of 1 to 2. The elementary bodies may, therefore, be divided, with respect to their *atomic specific heat*, into two classes, one class having just double the capacity for heat that the other class possesses. But if we employ the new instead of the old atomic weights ($H = 1$, $O = 16$; or $H = 0{\cdot}5$, $O = 8$), the specific atomic heat is the *same* for all elements; in other words, *the same quantity of heat is required to heat an atom of all simple bodies to the same extent. The product of the specific heat into the atomic weight is the atomic specific heat;* or, as Regnault terms it, *the atomic heat of the body.*

1324. In the following table (I.) the four gaseous elementary bodies, and bromine in its gasified state, are contrasted for the purpose of illustrating the preceding statements.

1. In column A the specific heat of equal weights of these elementary bodies is given, an equal weight of water being taken as unity.
2. In column B the atomic specific heats, the old atomic weights being employed.
3. In column C the atomic specific heats, the atomic specific heat of hydrogen being taken as 1.
4. In column D the old atomic weights.

5. In column E the atomic specific heats, the new atomic weights being employed.

6. In column F the atomic specific heats, atomic specific heat of hydrogen being taken as unity.

7. In column G the new atomic weights.

1325. It will be seen that there is a little deviation from the constant numbers in the case of chlorine and bromine; this might have been expected, as the specific heat of a body varies with its state, and chlorine is a condensable gas, the only one of the four gaseous elementary bodies, and bromine is a fluid body in its ordinary state.

1326. *Specific heat of atoms.*—If we compare the specific heat of the elements, not in *equal weights*, but in the ratio of their *atomic weights*, we find, if we employ the old atomic weights, they are resolved into two classes; and comparing the members of each class amongst themselves, we find they undergo, under these conditions, *an equal change of temperature for an equal quantity of heat.* But if we compare the members of the two classes together, we find that the members of the one class have *double* the capacity of heat that the others possess; but if we employ the new atomic weights ($H = 1, O = 16; H = 0·5, O = 8$) this difference vanishes, and all the elements then have, when taken in the proportion of their atomic weights, an equal capacity for heat.

Table I.

	A Specific heat. Equal weights. Water = 1.	B Atomic specific heats. Old atomic weights.	C Atomic specific heats. Atomic heat of H = 1.	D Old atomic weights.	E Atomic specific heats. New atomic weights.	F Atomic specific heats Atomic heat of H = 1.	G New atomic weights.
Hydrogen -	3·4046	3·4046	1	1	3·4046	1	1
Nitrogen	0·2440	3·3160	1	14	3·3160	1	14
Chlorine	0·1214	4·2097	1	35·5	4·2097	1	35·5
Bromine (gas)	0·0552	4·4160	1	80	4·4166	1	80
Oxygen	0·2182	1·7456	½	8	3·4912	1	16

1327. The intimate relation which exists between the specific heat of elementary bodies and their atomic weights was first pointed out by Dulong and Petit, and they deduced the law that *the specific heat of an elementary body is inversely as its atomic weight.* So that an atom of any simple substance, whether its volume be great or small, has the same capacity for heat, and requires the same quantity of heat to raise its temperature through a given number of degrees, as an atom of any other elementary substance. The subsequent investigations of Regnault on the specific heat of the elements did not confirm the universality of this law, if the old atomic weights were employed; for a small number of the elements were found, as we see by the table, to have an atomic heat double that of the other elements. The elements composing this class are hydrogen, nitrogen, chlorine, bromine, iodine, potassium, sodium, lithium, silver, gold, bismuth, arsenic, antimony, and phosphorus. Regnault has proposed to halve the atomic weights of the elements; if this were done, the atomic heat of all the elements would then be the same: but the same result would be attained if, instead of halving the atomic weights of the elements, to which there are objections in the case of phosphorus, arsenic, and antimony, we were to double those of the other elements. The student's attention has already been directed to these double atomic weights in the former part of this work, and it has there been shown that they accord better than the old weights, not only with physical data, but also with the chemical properties of these elements.

1328. We will now contrast the atomic heats of the solid bodies; and we see at once, from Table II., what might have been expected, that the constants obtained for the atomic specific heats of solids are not the same as those for the gaseous bodies. We see that the highest number for the atomic heats of solids is rather over 6, whilst the highest number for the gaseous bodies is a little over 3; but that the gaseous bodies whose atomic heats are a little over 3, would give, if they could be converted into the solid state, the atomic heat of 6, and *vice versâ*, is seen in the case of bromine; as a gas, its atomic heat (col. B) would, when corrected for irregularity, be a little more than 3; in the solid state its atomic heat (col.

B, Table II.) is a little more than 6. Adopting the old atomic weights, the elementary solid bodies, like the gaseous bodies, may be divided, with respect to their atomic specific heats, into two classes, one class having just double the capacity for heat that the other class possesses: but if we employ the new atomic weights, the specific atomic heat is the same for all the elements.

1329. In Table II. we have preserved the same order as in Table I.; it is unnecessary, therefore, to repeat the index to the table; but instead of taking, as in the former case, hydrogen as the standard, we have employed, in Table II., solid bromine as the standard.

TABLE II.*

0.16956

	A	B	C	D	E	F	G
	Specific heats. Equal weights. Water = 1.	Atomic specific heats. Old atomic weights.	Atomic specific heats. Atomic heat of Br = 1.	Old atomic weights.	Atomic specific heats. New atomic weights	Atomic specific heats. Atomic heat of Br = 1.	New atomic weights.
Bromine (solid) -	0·0843	6·744	1	80·	6·744	1	80·
Iodine - -	0·05412	6·8732	1	127·	6·8732	1	127·
Potassium -	0·1956	6·712	1	39·	6·712	1	39·
Sodium -	0·2934	6·748	1	23·	6·748	1	23·
Lithium † -	0·9408	6·5386	1	6·95	6·5386	1	6·95
Silver - -	0·05701	6·1571	1	108·	6·1571	1	108·
Gold - -	0·3244	6·3907	1	196·6	6·3907	1	196·6
Phosphorus	0·1887	5·8497	1	31·	5·8497	1	31·
Arsenic - -	0·0814	6·1050	1	75·	6·1050	1	75·
Antimony -	0·05077	6·0924	1	120·	6·0924	1	120·
Bismuth -	0·03244	6·5689	1	213·	6·5689	1	213·
Sulphur -	0·20259	3·2414	½	16·	6·4828	1	32·
Selenium -	0·0837	3·3145	½	39·6	6·6960	1	80·
Tellurium -	0·04737	3·031	½	64·	6·0620	1	128·
Magnesium	0·2499	2·9988	½	12·	5·9976	1	24·

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* In drawing up this table I have consulted M. Regnault's last Memoir "On the Specific Heat of some of the Simple Bodies" (*Annal de Chimie et de Physique*, 3rd Series, Tom. lxiii., 1861), as well as his earlier Memoirs.

† The specific heat of lithium, it will be observed, is almost equal to that of water.

TABLE II.—*continued.*

	A	B	C	D	E	F	G
	Specific heats. Equal weights. Water = 1.	Atomic specific heats. Old atomic weights.	Atomic specific heats. Atomic heat of Br = 1.	Old atomic weights.	Atomic specific heats. New atomic weights.	Atomic specific heats. Atomic heat of Br = 1.	New atomic weights.
Zinc - - -	0·0955	3·1054	½	32·5	6·2108	1	65·
Cadmium -	0·05669	3·1746	½	56·	6·3492	1	112·
Tin - - -	0·05623	3·3176	½	59·	6·6352	1	118·
Lead - -	0·0314	3·2499	½	103·5	6·4998	1	207·
Cobalt - -	0·1070	3·1565	½	29·5	6·3130	1	59·
Nickel - -	0·1086	3·2037	½	29·5	6·4074	1	59·
Iron - -	0·11379	3·1861	½	28·	6·3722	1	56·
Copper - -	0·09515	3·0162	½	31·7	6·0324	1	63·4
Mercury (solid) -	0·03192	3·192	½	100·	6·384	1	200·
Platinum -	0·03243	3·1943	½	98·5	6·3886	1	197·
Palladium -	0·05927	3·1413	½	53·	6·2826	1	106·
Iridium -	0·03259	3·2101	½	98·5	6·4202	1	197·
Rhodium -	0·05803	3·0175	½	52·	6·0350	1	104·
Osmium -	0·03063	3·0477	½	99·5	6·0954	1	199·
Tungsten -	0·03342	3·0746	½	92·	6·1492	1	184·
Molybdenum	0·07220	3·4656	½	48·	6·9312	1	96·
Manganese -	0·1217	3·2859	½	27·	6·5718	1	54·
Aluminum	0·2143	2·9359	½	13·7	5·8718	1	27·4

1330. The three elements, carbon, silicon, and boron, appear to form exceptions to the law of Dulong and Petit; but as they each form allotropic modifications, and as the specific heat of carbon, and probably that of the other two, varies with its allotropic modifications, it is difficult to decide which modification is to be regarded as the state in which the substance enters into combination: perhaps it may hereafter be found that each modification has a different atomic weight as well as a different specific heat. There are other difficulties attaching to the determination of the specific heat of silicon and boron; there is the difficulty of obtaining them perfectly pure: and in the case of boron there is another difficulty, which the student will learn on consulting Regnault's Memoir. The following table exhibits the specific and atomic heats of these three elements:—

	A Specific heats. Equal weights. Water = 1.	B Atomic specific heats. Old atomic weights.	D Old atomic weights.	E Atomic specific heats. New atomic weights.	G New atomic weights.
Diamond - - -	0·1468	0·8808	6	1·7596	
Graphite - - -	0·2018	1·2108		2·4216	12
Wood charcoal -	0·2415	1·4490		2·8980	
Silicon - - -	0·1774	3·7786	21·3	4·9672	28
Boron - - -	0·2500	2·7500	11·0	2·750	11

1331. In paragraph 193 we have placed before the student Sir B. Brodie's reasons for considering that, in certain compounds of carbon, the carbon is in the form of graphite; and he arrives at the conclusion that the number 33 is the atomic weight of the graphite. This view of the atomic weight of graphite is supported by its specific heat; for if we multiply the specific heat of graphite by 33, its atomic specific heat conforms to the law of Dulong and Petit, thus,—

$$0{\cdot}2018 \times 33 = 6{\cdot}6594.$$

1332. *Atomic heats of compound bodies.*—"Regnault has found that the specific heat of alloys is exactly the mean of that of their components, hence their atomic heat is equal to the sum of those of their components; but with this exception, the atomic heat of a compound body cannot be calculated, like its chemical equivalent, from the sum of the atomic heats of its constituents. The atomic heat of the compound is very generally less than that sum, and it varies from this number according as, during combination, condensation of the component particles has occurred to a greater or less extent, and according to other hitherto unascertained causes.

1333. "On comparing together equivalent quantities of isomorphous compounds possessed of a similar chemical composition, Neumann found that they likewise possessed equal atomic heats. The differences from the mean are in some cases considerable, but they are of the same order as those already observed to occur in the simple bodies. The mean atomic heat of the isomorphous carbonates, such, for example, as the carbonates of lime, baryta, iron, lead, zinc, strontia, and the double carbonates of lime and magnesia, is 10·61, varying from 10·55 and 10·85. In like manner, the sulphates of baryta, lime, strontia, and lead, yield a mean atomic heat of 12·41.

1334. "Regnault, from an extensive series of experiments on a great variety of compound bodies, has arrived at the conclusion that '*in all compound bodies of the same atomic composition, and of similar chemical constitution, the specific heats are inversely as the atomic weights.*' The product obtained by multiplying the specific heat into the equivalent number in any one class of compounds may, however, differ greatly from the product of the corresponding numbers in any other class, the numbers furnished by the different classes not being connected by any simple ratio.*" †

1335. *Development of heat by chemical action.*—The quantity of heat emitted by the combination of the same substances is always the same under the same circumstances. But the amount emitted cannot, in the majority of cases at least, be the actual quantities of heat due to the chemical action; because, as each change of state, and even each change in the state of aggregation, is attended with an evolution or absorption of heat, it follows that if the combination is attended with a change of state, or even with a change in the state of aggregation, there must be an addition to, or subtraction from, the amount of heat developed by the chemical action; for example, matter cannot pass from the solid to the fluid, or from the fluid to the gaseous state, without an absorption of heat; on the other hand, matter cannot pass from the gaseous to the fluid, or from the fluid to the solid state, without an evolution of heat. If matter only changes its state of aggregation, the change is generally attended with an evolution or absorption of heat; if the bulk of the body be diminished, for instance, heat will be evolved; if, on the other hand, it be increased, heat will be absorbed. The heat evolved must therefore exceed that really due to the act of combination in such cases as the following:—

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* This comparison is made with the old atomic weights.

† Miller's "Elements of Chemistry," 3rd vol.

1. When a gaseous compound occupies less bulk than its gaseous constituents did before combination.

2. When a liquid is produced by the combination of two gaseous compounds.

3. When a solid is produced by the combination of one solid and one gaseous substance, or by the combination of two gases; or by the combination of one solid and one liquid, or by the combination of two liquids.

1336. The heat evolved must be less than that really due to the combination in such cases as the following:—

1. When a liquid is produced by the combination of a liquid and a solid, or by the combination of two solids.

2. When a gaseous body is produced by the combination of a liquid and a gas, or by the combination of a gas and a solid.

1337. When a gaseous body is produced by the union of two gaseous bodies, and the compound occupies the same bulk that its constituents did before combination, even in this case the heat evolved might not be the actual quantity due to the combination, because the compound might have, and probably would have, a specific heat different to that of its elements.

1338. The heat of combination would be altered in quantity, not only by a change of state, or by a difference between the specific heat of the compound and that of its constituents, but also by the compound possessing a density greater or less than that of its elements.

1339. As we are unable to make corrections for these disturbing causes, we are unable to arrive at the true amount of heat evolved by the equivalents of the different elements.

1340. But little is known respecting the relation which the heat of combustion of a compound of two or more combustible substances bears to the sum of the heats of the combustion of its constituents. In some cases it is less than that sum (*e. g.*, marsh gas), in others greater (bisulphide of carbon, oil of turpentine). The relation in question is, doubtless, greatly affected by the molecular states of the compound and its elements in the separate state.

1341. As heat cannot be weighed or measured, the *absolute* amount of heat which any substance evolves in burning cannot be ascertained, but the *relative* amounts evolved by different substances can be accurately determined; this is accomplished by transferring the heat emitted by the combustion to a *third* body, and determining the number of degrees the given weight of this third body is raised in temperature by different substances: we thus arrive at the relative amounts of heat they evolve in the act of combining.

1342. La Place and Rumford were the earliest investigators in this interesting field of research; Lavoisier and La Place caused the heat to act on ice, and from the amount of ice melted they measured the amount of heat. The apparatus they employed in their investigations they termed a *calorimeter*. Ice is objectionable on account of the difficulty of obtaining the whole of the water produced by the liquefaction of the ice. Rumford, therefore, substituted water for ice, and although many improvements have been made on Rumford's method, water is still employed. We shall here give a description of the apparatus employed, and the method pursued by one of the latest and most successful investigators, Dr. Andrews,* in this difficult field of research.

1343. *Dr. Andrews' method.*—When the substances to be combined were in the gaseous state, and the products of combustion were also gaseous, the gases were mixed together in the proper proportions, as for a common eudiometric experiment, and were introduced into a copper vessel (Figs. 30 and 31), whose capacity was about 380 cubic centimetres. It was closed by a screw, as shown in the figure, the head of which is perforated with a conical aperture (the apex towards the outside), to admit a very tightly fitting cork. Through the cork a silver wire, *a a*, passes, and another, *b*, is soldered to the side of the screw. These wires, as shown in the figure, are connected by a very fine platina wire. When the vessel is closed (Fig. 30), the first silver wire is brought into contact with a narrow band of copper, *c c*, which surrounds the upper edge of the vessel, but is at the same time insulated from it.

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* "On the Heat Disengaged during the Combination of Bodies with Oxygen and Chlorine." By Thomas Andrews, M.D. *Philosoph. Mag.*, *May*, 1848.

1344. The vessel containing the mixed gases, and adjusted in the manner described, was introduced into another of larger capacity, which was then filled with water at the proper temperature. The latter was suspended in a cylinder having a moveable cover at both ends, and the whole was finally introduced into an outer vessel, also of a cylindrical shape, and which was capable of being rapidly rotated round its shorter axis. The whole arrangement will be understood by inspecting Fig. 32, in which the several parts of the apparatus are represented.

Fig.31.

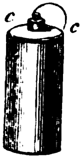


Fig.30.

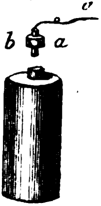
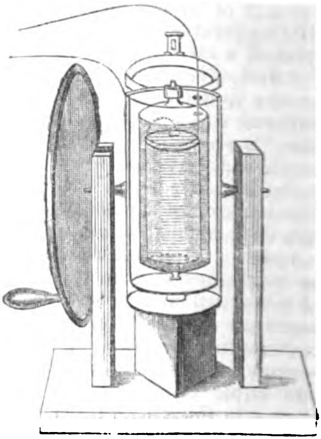


FIG. 32.



1345. Before observing the initial temperature, the apparatus was rotated for some time, in order to establish a complete uniformity of temperature through all its parts. The apparatus being fixed in the position shown in Fig. 32, the thermometer was next introduced through the apertures shown in the lids, and the temperature observed. On the removal of the thermometer, the exterior of the apparatus was brought into contact with one pole of a voltaic battery, while the other pole was passed through the water till it came into contact either with the central silver wire, or with the copper band (*c c*, Fig. 31.) The position of the wires at this period of the experiment is shown in Fig. 32. By this arrangement the circuit was completed through the fine platina wire, which, becoming instantly ignited, caused the mixture to explode. The orifice of the calorimeter was then quickly closed with a good cork, the lid of the outer vessel shut down, and the whole rotated for thirty-five seconds, in which short space of time the heat produced by the combination was found to be uniformly distributed through the apparatus. This rapid distribution of the heat was greatly facilitated by the presence of a small quantity of water in the inner vessel. The thermometer, previously brought as nearly as possible to the expected temperature of the liquid, was again introduced, and the increment of heat observed.

1346. The duration of the experiment was so short, that scarcely any correction for the cooling and heating influence of the air was required. The temperature of the air was in general a little above the mean between the initial and final temperatures of the apparatus. The heat, however, was given out so rapidly that the latter must have been nearly at the final temperature during the greater part of the time. After each experiment, the apparatus was again rotated for a period of thirty-five seconds, and the loss of heat from cooling observed. Dr. Andrews assumed one-half of this loss to be the required correction, except in the case of olefiant gas, when the initial temperature was a little lower than usual. The correction so applied, it will be seen, never exceeded 0·005° C.

1347. The thermal values of the different parts of the apparatus, in terms of water, were as follows:—

Copper,	170 grams.	× 0·095	16·15
Brass,	111 „	× 0·094	10·43
Solder,	15 „	× 0·043	0·64
Leather, cork, &c.			0·48
Thermal value			27·70

1348. The amount of water was always determined by weighing the apparatus with its contents after each experiment, and deducting the weight of the same when dry.

1349. *Determination of the heat disengaged during the* *combination of hydrogen and oxygen.*—The hydrogen employed was purified by passing it through a series of tubes in which it was successively exposed to solutions of acetate of lead, sulphate of silver, and hydrate of potash. It was afterwards collected over water in a graduated vessel. In this way it became contaminated with a small quantity of atmospheric air, the amount of which it was necessary to ascertain with precision. This was effected by an independent experiment, in which the gas was collected in exactly the same manner. In the case of other gases, the true volume was inferred from the diminution which occurred after the explosion. The difficulty, Dr. Andrews remarks, of obtaining accurate results in experiments upon gases collected over water (which for obvious reasons could not be avoided in this inquiry) is so well known to chemists, that it is unnecessary to dwell upon it. Dr. Andrews endeavoured in every case to determine by experiment, and to apply the necessary corrections for absorption, &c., but he has also given in his experiments the results immediately obtained by observation.

EXERCISES.

198. In the following experiments, H represents the volume of hydrogen gas in cubic centimetres as obtained by observation; H c, the same corrected for admixture of air, absorption by water, &c.; B, the height of the barometer in English inches, reduced to 0° C.; T, the temperature of the hydrogen gas in Centigrade degrees; E, the excess of the final temperature of the water in the calorimeter above the air; I, the increment of temperature found; I c, the same corrected; W, the weight of the water in the calorimeter expressed in grammes; and V, the thermal value of the vessels.

	1st Experiment.	2nd Experiment.
H	229·3 c. c.	229·2 c. c.
H c	226·8 c. c.	226·7 c. c.
B	30·17 in.	30·16 in.
T	19°·7	19°·8
E	0°·9	0°·9
I	2°·074	2°·063
I c	2°·079	2°·068
W	275·7 grams.	278·7 grams.
V	27·7 grams.	27·7 grams.

Determine from these numbers the heat evolved during the combination of one litre of *dry* hydrogen gas measured at 0° C., and under a pressure of 29·92 in., with oxygen, in each of the experiments; and, taking the mean of the two numbers so found, find the heat produced during the combination of one gramme of oxygen with hydrogen.

1350. The heat obtained in the union of oxygen and hydrogen arises from two distinct causes: one, the chemical combination; the other, the condensation of the vapour formed by the combination. The latter is an accidental complication, which would not have interfered with the result if the experiment had been performed at a temperature superior to 100° C. If we assume the latent heat of steam at 20° to be 611 units, the heat evolved by the condensation of 1·125 grammes steam will be 687, which, deducted from the numbers found for the heat produced by the combination of 1 gramme of oxygen with hydrogen, gives the true heat due to the chemical combination of that weight of oxygen with hydrogen.

1351. *Determination of the heat disengaged during the combination of carbonic oxide and oxygen.*—The carbonic oxide was prepared by the action of sulphuric acid on oxalic acid, the carbonic acid formed during the process being absorbed by a solution of caustic potash. To insure complete combustion, an excess of oxygen was always employed. The residual gas, after being deprived of its carbonic acid, was measured, and the original volume of carbonic oxide was deduced from the reduction of volume of the mixture after combustion. As before, Dr. Andrews endeavoured to correct the volumes actually found for the errors inevitable to eudiometric experiments performed over water. A small allowance was also made for the air extracted from the water (about 20 grammes), which was always left in the inner vessel.

199. In this and Exercises 200 and 201, M designates in cubic centimetres the volume of the gaseous mixture before combustion; M c, the same corrected for absorption by water during the transference from one vessel into another, &c.; R, the volume of the residue (consisting chiefly of the excess of oxygen) after combustion, and removal of the carbonic acid; R c, the same corrected. The other letters

have the significations already explained in the previous exercise.

	1st Experiment.	2nd Experiment.
M	362·2 c. c.	362·5 c. c.
M c	361·3 c. c.	361·6 c. c.
R	24·2 c. c.	24·2 c. c.
R c	24·3 c. c.	24·3 c. c.
B	30·09 in.	30·09 in.
T	15°·7	15°·8
E	1°·0	0°·9
I	2°·148	2°·132
I c	2°·153	2°·137
W	270·7 grams.	272·0 grams.
V.	27·9 grams.	27·9 grams.

Determine from these numbers the heat evolved during the combination of one litre of dry carbonic oxide gas, measured at 0°, and under a pressure of 29·92 inches, with oxygen in each of the experiments; and, taking the mean of the two numbers so found, find the heat produced during the combination of one gramme of oxygen with carbonic oxide.

1352. *Determination of the heat disengaged during the combination of marsh gas with oxygen.*

200. The marsh gas employed in these experiments was obtained from a stagnant pool. It contained an unusually large proportion of nitrogen. A large excess of oxygen was employed to burn it.

	1st Experiment.	2nd Experiment.
M	360·2 c. c.	359·0 c. c.
M c	359·3 c. c.	358·1 c. c.
R	105·0 c. c.	108·5 c. c.
R c	105·8 c. c.	109·4 c. c.
B	30·10 in.	30·10 in.
T	15°·8	15°·7
E	1°·0	1°·0
I	2°·504	2°·457
I c	2°·509	2°·462
W	268·1 grams.	268·7 grams.
V	28·1 grams.	28·1 grams.

Determine from these numbers the heat evolved during the combination of one litre of dry marsh gas, measured at 0° C., and under a pressure of 29·92 inches, with oxygen in each of the experiments; and, taking the mean of the numbers so found, find the heat produced during the combination of one gramme of oxygen with marsh gas, and then apply a similar correction for the heat produced by the condensation of the vapour of water to that employed in exercise (198).

1353. *Determination of the heat disengaged during the combination of olefiant gas with oxygen.*

201. The olefiant gas employed in the experiments was prepared and purified by the usual processes. It was still found to contain 6·4 vols. of carbonic oxide in every 100 vols., in accordance with the observation first made by Dr. J. Davy. It is necessary, in reducing the results, to take into account the heat produced by the combustion of this portion of carbonic oxide. In order to insure the complete combustion of the gas, and at the same time to diminish the force of the explosion, nearly four and a half volumes of oxygen were taken for every volume of olefiant gas.

	1st Experiment.	2nd Experiment.
M	364·8 c. c.	364·0 c. c.
M c	363·9 c. c.	363·1 c. c.
R	110·3 c. c.	106·4 c. c.
R c	111·2 c. c.	107·3 c. c.
B	30·15 in.	30·23 in.
T	13°·6	13°·3
E	0°·8	1°·0
I	3°·015	3°·163
I c	3°·017	3°·166
W	265·3 grams.	255·7 grams.
V	28·1 grams.	28·1 grams.

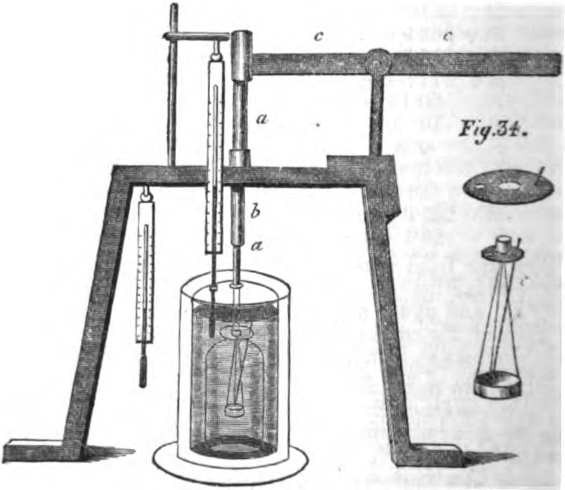
Determine from these numbers the heat evolved during the combination of one litre of dry olefiant gas, measured at 0° C., and under a pressure of 29·92 in., with oxygen, in each of the experiments; and, taking the mean of the two numbers so found, find the heat produced during the combination of one gramme of oxygen with olefiant gas; and then apply a similar correction for the heat produced by the condensation of the vapour of water to that employed in exercise (198).

1354. *Combination of oxygen with solid and fluid bodies.*

—A considerable modification of the apparatus was required for the determination of the heat produced during the combination of solid and liquid substances with oxygen. The slowness of the combustion in most cases, made it necessary to operate upon a larger scale; and as the apparatus could no longer be inverted, it was also necessary to distribute the heat by a different method.

1355. Fig. 33 exhibits the general form of the apparatus. The combination took place in a copper vessel of about four litres capacity. The combustible was placed in a platina cup, shown in Fig. 34, which is suspended from the lid of the copper vessel by means of platina wires. A fourth wire, also of platina, but insulated by being surrounded by a glass tube, descends through an opening in the lid, and is connected below with the platina cup through the medium of a very fine platina wire, and above with a circular disc of copper, which is seen detached in Fig. 34, and in its proper position in Fig. 33. Before the commencement of an experiment,

FIG. 33.



this disc was firmly fixed to the lid of the copper vessel, but it was also carefully insulated from it. Thus by bringing the disc and any other part of the copper vessel into contact with the opposite poles of a voltaic battery, the fine platina wire could be instantly ignited.

1356. In performing an experiment, the copper vessel was first filled with pure oxygen gas, the lid carrying the platina cup, &c., then introduced into its place, the copper disc attached to the lid, and its metallic connection with the insulated wire, *c*, carefully secured. The whole was next placed in the calorimeter, which contained the proper quantity of water, previously cooled to the required temperature, and weighed. The inner vessel was secured in its place by the vertical rod, *a a*. The calorimeter was covered with a lid containing apertures for the vertical rod and the thermometer, and the whole was surrounded by an outer vessel of tin plate, to prevent the effects of radiation. The details of the arrangement will be obvious from an inspection of Fig. 33. By means of the horizontal arm, *c c*, the inner vessel could be agitated through the water in the calorimeter. A pin, shown at *b*, restrained the motion of the vertical rod within such limits that the inner vessel was never permitted to rise during the agitation above the surface of the water in the calorimeter. Upon the sides and bottom of the inner vessel, small hollow knobs were placed, which maintained at all times a certain distance between the two vessels.

1357. Previous to the commencement of an experiment, the inner vessel was gently moved up and down till every part of the apparatus had acquired the same temperature. The ignition was effected by a similar method to that already described in the previous section, by bringing the vertical rod and the copper disc respectively into contact with the terminal wires of a galvanic arrangement. The same aperture in the lid served for the introduction of the thermometer, and, afterwards, of the galvanic wire. After the combination had begun, the inner vessel was gently moved up and down within the calorimeter for a sufficient period of time to allow, not only the combustion to be completed, but the heat thereby produced to be uniformly distributed through the whole of the apparatus. In every experiment, after the observation of the final temperature, the agitation was again repeated during two minutes, in order to ascertain positively that the whole of the heat had been obtained.

1358. The longer period of time occupied in these experiments rendered the corrections for the cooling and heating influence of the air of more importance than in the former observations. To determine with absolute accuracy the value of these corrections, under the varying circumstances of each experiment, would have been extremely difficult. Dr. Andrews therefore endeavoured so to arrange the experiments that the amount of correction to be applied in each case might be very small; so small, indeed, that the application of an imperfect approximation might be practically sufficient. From the effects of friction, the proximity of the person of the observer, and other causes, the rate of heating was always greater than the rate of cooling, for equal differences between the temperature of the air and of the apparatus; and for the same reasons, the latter was found to maintain a stationary temperature only when the thermometer in it indicated a temperature about $0^\circ{\cdot}3$ C. higher than that of the surrounding air. If we represent by a the difference between the temperature of the air and of the apparatus, the correction, V, for the gain or loss of heat sustained by the apparatus during m minutes, will be expressed by the formula,—

$$V = \mp m\,(a \pm 0^\circ{\cdot}3)\,0^\circ{\cdot}0025.$$

1359. The values of V given by this expression agree, within the ranges of temperature which occurred in these experiments, very closely with the direct results of observation.

1360. The usual time which elapsed between the observation of the initial and final temperatures was sixteen minutes; and in such cases it was assumed that the apparatus was at the minimum temperature during one-and-a-half minute, at the maximum during eight minutes, and during the intermediate period at the temperature of the air. In other cases, where the combination took place more quickly, the corrections were made on the assumption that the apparatus was at the minimum point during one minute, and at the maximum during one-half of the whole time occupied by the experiment.

EXERCISES.

1361. *Determination of the heat disengaged during the combination of carbon and oxygen.*—The carbon was employed in the form of wood-charcoal. It was purified by the method of M. Dumas from all oxidable matters, first by ebullition in strong nitro-muriatic acid, and afterwards by exposure for several hours at a strong red heat to the action of dry chlorine gas. To expel all volatile compounds, it was finally exposed to a strong white heat under a layer of charcoal. The earthy impurities, together with a certain portion of carbon (which, notwithstanding the great excess of oxygen, always escaped combustion), remained in the platina dish after each experiment. By deducting the weight of this residue from that of the carbon originally taken, the weight of the carbon consumed was immediately obtained. To obtain with accuracy the weight of the charcoal, it was introduced in the state of fine powder into the platina cup already referred to; and after being heated nearly to ignition, the latter was enclosed in a copper box, which, when covered by its lid, communicated with the external air only by a very small aperture. The whole was then allowed to cool *in vacuo* over sulphuric acid; and when cold, a stream of dry air was admitted into the receiver. The aperture in the lid being now closed, the weight of the entire was determined.

1362. To obtain complete combustion a very large excess of oxygen was employed; but even with this precaution, carbonic oxide was discovered in the residual gas in several of the following experiments.

202. In this and the two following exercises, M designates the weight of the substance burned; T, the temperature of the air, and the other letters the same quantities as in the previous exercises,

	1st Experiment.	2nd Experiment.
M	1·088 grams.	1·177 grams.
T	10°·6	10°·4
E	0°·3	0°·5
I	2°·473	2°·648
Ic	2°·464	2°·644
W	3183 grams.	3214 grams.
V	180 grams.	180 grams.

Determine from these numbers the heat evolved during the combination of one gramme of carbon with oxygen, and one gramme of oxygen with carbon.

1363. Dr. Andrews remarks that these numbers cannot be considered perfectly accurate, but are probably a little below the truth, in consequence of the formation of the small quantity of carbonic oxide, to which reference has already been made.

1364. *Determination of the heat disengaged during the combination of sulphur and oxygen.*

203. The sulphur was employed in the state of flowers of sulphur, deprived of the acid with which they are always contaminated, by washing. A small quantity of earthy residuum remained, the weight of which was determined at the end of each experiment, and deducted from the original weight of the sulphur. During the combustion, a small quantity of sulphuric acid (corresponding to about 3 per cent. of the sulphur) was formed, for which reason the experimental results must indicate a little more than the true quantity of heat due to the conversion of sulphuric into sulphurous acid. The heat in these experiments was given out in the course of eight minutes.

	1st Experiment.	2nd Experiment.
M	3·087 grams.	3·089 grams.
T	10°·4	12°·8
E	1°·0	1°·0
I	2°·51	2°·436
I c	2°·512	2°·438
W	2699 grams.	2739 grams.
V	175 grams.	175 grams.

Determine from these numbers the heat evolved during the combination of one gramme of sulphur with oxygen and one gramme of oxygen with sulphur.

1365. *Determination of the heat disengaged during the combustion of alcohol in oxygen.*

204. The alcohol employed in the experiment was perfectly pure. Its density at 15° was 0·7959, and it was always redistilled from a large excess of pure lime im-

mediately before being used. The principal difficulty, Dr. Andrews remarks, in examining the heat produced by the combustion of this substance, was to complete all the preliminary arrangements after its introduction into the oxygen gas so as to ignite it before any appreciable quantity had evaporated. The shortest time in which Dr. Andrews was able to accomplish this was seven minutes; but there can be little doubt, he adds, that any portion of alcohol which might rise into the state of vapour during this time would become ignited along with the rest. The duration of each experiment was five minutes.

	1st Experiment.	2nd Experiment.
M	1·060 grams.	0·890 gram.
T	9°·4	10°·1
E	1°·4	0°·7
I	2°·555	2°·04
I c	2°·558	2°·039
W	2686 grams.	2773 grams.
V	174 grams.	174 grams.

Determine from these numbers the heat evolved during the combination of one gramme of alcohol with oxygen and one gramme of oxygen with alcohol.

1366. For the modification of the apparatus employed by Dr. Andrews in determining the heat disengaged during the combination of bodies with *chlorine*, we must refer the student to Dr. Andrews' memoir. We will now give a tabular statement of the results arrived at by Dr. Andrews, and also by Favre and Silbermann.*

1367. "The following table is compiled chiefly from the results of Dulong, Andrews, and Favre and Silbermann. It is founded upon the direct results obtained by the rapid combustion, in oxygen, of the various substances enumerated in the first column. The *heat unit* adopted is the one proposed by Dulong, viz., the quantity of heat required to raise one gramme of water 1° C., or rather from 0° C. to 1° C. The second column indicates the units of heat evolved during the act of combustion; or the weight in grammes of water which would be raised from 0° C. to

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* The student is referred to M. Favre and Silbermann's Memoir, *Annal. de Chimie*, 3rd Series, tom. xxxiv., 1852, for a description of the apparatus they employed in their researches.

1° by the combustion of one gramme of each substance. The third column indicates the weight of water heated to the same amount by the combination of one gramme of oxygen with each body. And the fourth column (the *calorific equivalent*) is obtained by multiplying the numbers in the third column by 8 (the equivalent number of oxygen).

Heat developed during the combustion in oxygen.

Substances burned.	Heat Units.	Grammes of water raised 1° C. by combination of 1 gramme of oxygen.	Calorific equivalent.	Compound formed.	Observer.
	Grammes of water raised 1° C. by 1 gramme of each substance.		Grammes of water raised 1° C. for 8 grammes (1 eq.) of oxygen.		
Hydrogen	34,462	4,307	34,462	HO	Favre and Silbermann.
"	33,808	4,226	33,808	"	Andrews.
"	34,743	4,343	34,743	"	Dulong.
Carbon	8,080	3,030	24,240	CO_2	Favre and Silbermann.
"	7,900	2,962	23,696	"	Andrews.
"	7,912	2,967	23,736	"	Despretz.
Sulphur	2,220	2,220	17,760	SO_2	Favre and Silbermann.
"	2,307	2,307	18,456	"	Andrews.
"	2,601	2,601	20,808	"	Dulong.
Phosphorus	5,747	4,509	36,072	PO_5	Andrews.
"	5,669	...	...	"	Abria.
Zinc	1,301	5,285	42,282	ZnO	Andrews.
"	1,298	5,273	42,185	"	Dulong.
Iron	1,576	4,134	33,072	F_3O_4	Andrews.
"	1,702	4,340	34,720	"	Dulong.
Cobalt	1,080	3,995	31,960	?	"
Nickel	1,006	3,723	29,784	NiO	"
Tin	1,233	4,545	36,360	SnO_2	"
"	1,144	4,230	33,519	"	Andrews.
Antimony	961	5,875	47,000	SbO_4	Dulong.
Copper	602	2,394	19,152	CuO	Andrews.

Heat developed during the combustion in oxygen—(continued).

Substances burned.	Heat Units.		Calorific equivalent.	Compound formed.	Observer.
	Grammes of water raised 1° C. by 1 gramme of each substance.	Grammes of water raised 1° C. by combination of 1 gramme of oxygen.	Grammes of water raised 1°C. for 8 grammes (1 eq.) of oxygen.		
Copper	632	2,512	20,096	Cu O	Dulong.
Carbonic oxide	2,634	4,609	36,876	$C\,O_2$	,,
,,	2,431	4,258	34,034	,,	Andrews.
,,	2,403	4,205	33,642	,,	Favre and Silbermann.
Protoxide of tin	534	4,473	35,784	$Sn\,O_2$	Dulong.
,,	521	4,349	34,792	,,	Andrews.
Suboxide of copper	256	2,288	18,304	Cu O	,,
,,	244	2,185	17,480	,,	Dulong.
Cyanogen	5,195	4,221	33,768	...	,,
Marsh gas	13,063	3,266	26,128	...	Favre and Silbermann.
,,	13,185	3,296	26,368	...	Dulong.
,,	13,108	3,277	26,216	...	Andrews.
Olefiant gas	11,942	3,483	27,864	...	,,
,,	11,858	3,458	27,664	...	Favre and Silbermann.
,,	12,030	3,514	28,112	...	Dulong.
Alcohol	6,909	3,311	26,488	...	,,
,,	6,850	3,282	26,256	...	Andrews.
,,	7,183	3,442	27,536	...	Favre and Silbermann.
Ether	9,027	3,480	27,840	...	,,
Olive oil	9,862	...	...	...	Dulong.
Oil of turpentine	10,852	3,294	26,352	...	Favre and Silbermann.

"1368. The following tables contain the results of a similar series of experiments, in which chlorine, bromine, and iodine were employed instead of oxygen,—

Quantities of heat disengaged by the action of chlorine.

Elements operated on.	Grammes of water raised 1° C. by combination of 1 gram. of substance.	Grammes of water raised 1° C. by combination of 1 gram. of chlorine.	Grammes of water raised 1° C. by combination of 1 eq. (35·5 grammes) of chlorine.	Compound produced.	Observer.
Hydrogen	24,087	678	24,087	HCl	Abria.
„	23,783	670	23,783	„	Favre and Silbermann.
Phosphorus	3,422	607	21,548	PCl_5	Andrews.
Potassium	2,655	2,943	104,476	KCl	„
Zinc	1,529	1,427	50,658	$ZnCl$	„
Iron	1,745	921	32,695	Fe_2Cl_3	„
Tin	1,079	897	31,722	$SnCl_2$	„
Antimony	707	860	30,401	$SbCl_3$	„
Arsenic	994	704	24,992	$AsCl_3$	„
Copper	961	859	30,494	$CuCl$	„
Mercury	?	822	29,181	?	„

Quantities of heat disengaged by the action of bromine and iodine.

Elements operated on.	Grammes of water raised 1° C. by combination of 1 gram. of substance.	Grammes of water raised 1° C. by combination of 1 gram. of chlorine.	Grammes of water raised 1° C. by combination of 1 eq. of bromine or iodine.	Compound produced.	Observer.
			Bromine.		
Zinc	1,269	508	40,640	$ZnBr$	Andrews.
Iron	1,277	298	23,833	Fe_2Br_3	„
			Iodine.		
Zinc	819	209	26,617	ZnI	„
Iron	463	63	8,046	Fe_2I_3	„

1369. The results of the earlier experimenters on the heat of combination led Welter to consider it as a law, that a given quantity of oxygen evolves the same quantity of heat, with whatever body it may combine. This supposition the student will see, from the table just given, is not confirmed by the results of the more recent experimenters, although the quantities evolved by the combination of a constant weight of oxygen with different combustible bodies are much more nearly equal than the quantities evolved by the combination of equal weights of these several bodies with oxygen.

1370. The student will see, on comparing the quantities of heat evolved by different substances in combining with an equivalent of oxygen, and the quantities evolved by the same substances in combining with an equivalent of chlorine, that the heat evolved in the combination of a substance with chlorine is in some cases greater, and in others less, than in the combination of the same substance with oxygen. "The numbers do not exhibit any simple relation to each other, so that no conclusion can be drawn from them as to the quantity of heat evolved or absorbed in the substitution of chlorine for oxygen, or of one metal for another, in combination with either of these elements. Here, as in other cases, the difference in the state of aggregation doubtless interferes with the constancy of action which might otherwise be observed. The amount of interference arising from this cause is much diminished when compounds are compared in the state of aqueous solution; and, accordingly, it is found that when the quantities of heat evolved by the combination of different bases and acids (or metals and radicals), in the form of soluble salts, are compared, numbers are obtained which exhibit a tolerably near approach to regular progression."

1371. The heat developed by the combination of an oxidized body with oxygen—as, for instance, carbonic oxide or protoxide of tin with oxygen—is less, as might be expected, than that produced in the complete oxidation of the substance, as carbon or tin, for example. The student will see by the table at page 609, that 2,403 units of heat are evolved in the conversion of one gramme of carbonic oxide into carbonic acid, consequently 5,607 units of heat will be evolved in the conversion into carbonic acid of *that* *quantity* of carbonic oxide which contains *one gramme of carbon*. On the other hand, in the conversion of *one gramme of carbon* into carbonic acid, 8,080 units of heat are evolved. Therefore, in the conversion of one gramme of carbon into *carbonic oxide* (8080 — 5607 =) 2473 units of heat are evolved. So that in the conversion of carbon into carbonic oxide less than half the amount of heat is evolved than is produced in the conversion of the same element into carbonic acid. This is probably owing to a quantity of the heat being rendered latent by reason of the solid carbon assuming the gaseous state.

1372. *Influence of dimorphism.*—Different quantities of heat are evolved by sulphur in its different allotropic conditions: in the conversion into sulphurous acid of the octohedral form, 2,220 units of heat are evolved; in the conversion of the prismatic form, 2,264 units are evolved; and in the conversion of the viscous form, 2,258 units are evolved.* It is generally the case that of two or more modifications of the same substance the form which has the greatest specific heat evolves also the greatest amount of heat of combination. Thus, the specific heat of yellow phosphorus is greater than that of the red variety, one gramme of the yellow evolves 5,953 units, and one gramme of red evolves 5,070 units of heat in its conversion into phosphoric anhydride. "The same relation is strikingly shown by the following comparison of the quantities of heat evolved in the complete combustion of equal weights of different kinds of carbon, as determined by Favre and Silbermann, with their specific heats, as determined by Regnault:"—

	Heat of combustion.	Specific heat.
Wood charcoal - - -	8,080 -	0·24150
Coke from gas retorts - -	8,047 -	0·20360
Native graphite - - -	7,797 -	0·20187
Graphite from blast furnaces	7,762 -	0·19702
Diamond - - - -	7,770 -	0·11687

A remarkable fact was observed in respect to diamond, namely, the change effected in its calorific power by heating it to 400° C. or 500° C., and then allowing it to cool before burning it. Thus, the calorific power, before the preliminary heating, was 7770·1, and afterwards 7878·7, the difference being 108·6.

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* These different forms also differ in their specific gravity; the specific gravity of the octohedral form is 2·05, that of the prismatic 1·955, and that of the viscous 1·957.

1373. *Heat developed on the combination of acids and bases.*—Dr. Andrews* has determined the heat evolved during the union of bases and acids; in order to avoid the complex effects that arise when successive combinations and decompositions of different kinds occur in the same chemical action, he diluted the solutions of the acids and bases largely with water previous to examining their thermal reactions, and the result fully realized his anticipations. The general conclusion Dr. Andrews deduced from his investigation may be briefly expressed by stating that *the heat developed during the union of acids and bases is determined by the base and not by the acid.* The following special laws will be found to comprehend the greater number of cases of chemical action to which the foregoing principle can be made to apply:—

1. An equivalent of the same base, combined with different acids, produces *nearly* the same quantity of heat.

2. An equivalent of the same acid, combined with different bases, produces different quantities of heat.

3. When a neutral salt is converted into an acid salt by combining with one or more equivalents of acid, no disengagement of heat occurs.

4. When a double salt is formed by the union of two neutral salts, no disengagement of heat occurs.

5. When a neutral salt is converted into a basic salt, the combination is accompanied by the disengagement of heat.

6. When one and the same base displaces another from any of its neutral combinations, the heat evolved or absorbed is always the same, whatever the acid element may be.

1374. As some of the bases (potash, soda, baryta, and strontia) form what we may, perhaps, designate an isothermal group, such bases will develop the same, or nearly the same heat in combining with an acid, and no heat will be developed during their mutual displacements.

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* Dr. Andrews' "Report on the Heat of Combination," in the *Report of the British Association* for 1849.

1375. The base Dr. Andrews employed for displacing the others was the hydrate of potash in a state of dilute solution of known strength. The changes of temperature, referred to 1,000 parts of water, were found to be, with salts of

Lime	—0·36°	Oxide of zinc	+ 1·74°
Baryta	0·0	Protoxide of mercury	+ 1·86
Strontia	0·0	Protoxide of lead	+ 2·82
Soda	+ 0·08	Protoxide of copper	+ 3·00
Ammonia	+ 0·74	Oxide of silver	+ 3·93
Manganese	+ 1·07	Peroxide of iron	+ 4·09
Protoxide of iron	+ 1·60		

1376. The above laws are not intended, Dr. Andrews observes, to embrace the thermal changes which occur during the conversion of an anhydrous acid and base into a crystalline compound. The steps by which such a conversion is effected are generally very complicated, and involve successive combinations and decompositions. We cannot combine, at ordinary temperatures, a dry acid and a dry base; and when combination takes place in presence of water, hydrates of the acid and base are first formed, which are afterwards decomposed, and the crystalline salt finally obtained is sometimes anhydrous, sometimes combined with water. To expect simple results where so many different actions must produce each its proper thermal effect would be altogether vain; and to introduce the consideration of some of these actions without the whole, would only render the numbers empirical. In the experiments from which the foregoing laws were deduced, the acids and bases before combination, and the compounds after combination, were as nearly as possible in the same physical state. The only change which occurred was the combination of the acid and base, and the heat evolved must, therefore, have arisen from the act of combination. Such changes of temperature as are produced by solution are not in any way concerned in producing these thermal effects, as none of the reacting bodies assumed at any time the solid state. The insoluble bases form, it is true, an unavoidable exception to this statement, and in the experiments with them the results would require to be corrected for the heat due to the change of the base from the solid to the fluid state. As this correction, however, although unknown, must be a constant quantity for the same base, it would not, if applied, interfere with the direct proof of the first law.

1377. *Metallic substitutions.*—The general result of Dr. Andrews' investigation on metallic substitutions may be thus expressed:—"When an equivalent of one and the same metal replaces another in a solution of any of its salts of the same order, the heat developed is always the same; but a change in either of the metals produces a different development of heat." This is evidently an analogous law to that already stated for the thermal changes which accompany basic substitutions.

1378. "The following are the numbers given by Andrews, but he has purposely abstained from any attempt to deduce from them the amount of heat developed during the indirect oxidation of the metal which acts as the precipitant:—

Table of heat evolved during metallic precipitations.

Class of salts used, and metals employed for precipitating them.	Name of precipitated metal.	Units of heat evolved by precipitated metal.		Name of precipitating metal.	Units of heat for 1 gramme of precipitating metal.
		For 1 grm.	For 1 equivalent		
Salts of copper by zinc -	Copper	866	27,452	Zinc	847
Salts of copper by iron -	Copper	592	18,736	Iron	677
Salts of copper by lead -	Copper	268	8,488	Lead	82
Salts of silver by zinc -	Silver	426	45,976	Zinc	1,420
Salts of silver by copper	Silver	161	17,408	Copper	549
Salts of lead by zinc -	Lead	182	18,856	Zinc	585
Salts of mercury by zinc	Mercury	333	33,328	Zinc	1,034
Salts of platinum by zinc	Platinum	899	88,680	Zinc	2,750

1379. "If the metals be arranged in a list, beginning with those which emit the largest amount of heat when used as precipitates, the order in which they will stand is the following:—Zinc, iron, lead, copper, mercury, silver, and platinum. Now it will be remarked that this is exactly in the electro-chemical order, zinc being the most electro-positive, and platinum the most electro-negative. Another interesting point of connection between the thermal and the electrical phenomena exhibited by the metals, is to be observed in the fact that the nature of the acid contained in the salt which is undergoing decomposition does not influence either its thermal equivalent or the electro-motive force which it exerts when employed in the production of voltaic action.

1380. "Another remarkable conclusion has been deduced by Andrews from these experiments:—If three metals, A, B, and C, be so related that A is capable of displacing B and C from their combinations, and B be also capable of displacing C, the heat developed by the substitution of A for C will be exactly equal to that developed in the substitution of A for B, together with that developed in the substitution of B for C. Thus,—

	Heat units.
1 equivalent of lead displaced by zinc =	18,856
1 equivalent of copper by lead - - =	8,488
1 equivalent of copper by zinc - - =	27,344
The experimental number being -	27,452

1381. "An analogous phenomenon is observed in the electrical relations of the metals. When three metals, such as platinum, zinc, and potassium, are arranged two and two in their electrical order, the electro-motive force generated between the two extremes, platinum and potassium, is equal to the sum of the electro-motive forces of the pairs, platinum and zinc and zinc and potassium."[*]

1382. Heat is evolved in the combination of acids with water; the greatest amount of heat is developed in the combination of the acid anhydride with water; the heat decreases as the acid combines with each additional atom of water. Thus,—

			Units of heat.
SO_3	gives with	HO	12,432
HO, SO_3	,,	HO	3,108
$2HO, SO_3$	,,	HO	1,554
$3HO, SO_3$	,,	$3HO$	1,554
$6HO, SO_3$	,,	xHO	1,554

1383. When a gas dissolves in water heat is evolved, partly in consequence of the chemical combination, and partly in consequence of the condensation of the gas.

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[*] Miller's "Elements of Chemistry," 3rd vol.

1384. If, on the solution of a salt or other solid compound in water, combination takes place between the compound and some of the water, heat is developed; but if no combination takes place, the solution is generally attended with a reduction of temperature, owing to heat being absorbed in the passage from the solid to the liquid state. Anhydrous chloride of calcium combines with water, forming the hydrate, $Ca\,Cl + 6\,H\,O$, the combination being attended with great evolution of heat; but the solution of the hydrate in water produces cold.

1385. *Combustion of polymeric compounds.*—1 gramme of marsh gas evolved 13,063 heat units. Compounds of the formula $n\,(C_2\,H_2)$ gave the following values:—

		Heat units.
Olefiant gas	$C_4\,H_4$	11,858
Amylene	$C_{10}\,H_{10}$	11,491
Paramylene	$C_{20}\,H_{20}$	11,303
The compound	$C_{22}\,H_{22}$	11,262
Cetene	$C_{32}\,H_{32}$	11,078
Metamylene	$C_{40}\,H_{40}$	10,928

1386. From this table it will be seen that the heat of combustion diminishes the oftener the group of atoms, $C_2\,H_2$, enters into the compound. Favre and Silbermann infer that each addition of $C_2\,H_2$ causes a decrease of 37·5 heat units. Calculating the heat of combustion of olefiant gas in this way, we find that it differs from the experimental result; but this is explained by the fact that the *calculation* is based upon data afforded by the combustion of liquids, and consequently the quantity of heat required to retain the compound in the gaseous state ought to be added.

1387. *Combustion of ethers and alcohols.*—Common ether evolved 9027·6 heat units; amylic ether, 10188; methylic alcohol, 5307·1; common alcohol, 7183·6; amylic alcohol, 8958·6; and cetylic alcohol, 10629·2. From these data a table has been constructed for the various bodies of the series $n\,(C_2\,H_2) + 2\,H\,O$.

1388. *Combustion of the fatty acids.*—Formic acid evolved 2091; acetic acid, 3505·2; butyric acid, 5647·0; valerianic acid, 6439·0; cetylic acid, 9316·5; stearic acid, 9716·5. From these data a table has been constructed for this class of bodies, the general formula for which may be represented $n\,(C_2H_2) + O_4$.

1389. *Combustion of the compound ethers.*—We will give the results obtained by the combustion of some of these bodies:—Formiate of methyl evolved 4197·4; acetate of methyl, 5342·0; formiate of ethyl, 5278·8; acetate of ethyl, 6292·7; butyrate of methyl, 6791·5; butyrate of ethyl, 7090·9. These bodies may be represented by the general formula $n\,(C_2H_2) + O_4$; they are isomeric with the fatty acids. The student will see, from a comparison of the number of heat units evolved by this and the preceding class, that bodies isomeric in composition do not evolve equal quantities of heat in combustion. This conclusion is confirmed by the following examples:—

Compound.		Heat of combustion.
Terebene	$C_{20}H_{16}$	- - - 10,662
Oil of turpentine	$C_{20}H_{16}$	- - - 10,852
Oil of lemons	$C_{20}H_{16}$	- - - 10,959

1390. Several of the preceding examples have shown that the calorific power of a substance is not always the mean of that of its elements; we find it is not the mean in marsh gas, but that it is nearly the mean in olefiant gas: thus,—The calorific power of marsh gas by its combustion in oxygen was found to be 13,063. Now the relation in weight between the carbon and hydrogen in this compound is as 3 : 1. If, therefore, its calorific power were the mean of that of its elements, the number would be $(8080 \times 3 + 34462) \div 4 = 14675{\cdot}5$. The calorific power of olefiant gas was found to be 11857·8. Now the relation in weight between the carbon and hydrogen in this compound is as 6 : 1. If, therefore, its calorific power were the mean of that of its elements, the number would be $(8080 \times 6 + 34462) \div 7 = 11848{\cdot}8$.

1391. *Cold produced by chemical decomposition.*—As heat is evolved in the combination of bodies, we should naturally expect that there would be an absorption of heat in the decomposition of bodies. This is found to be the case, although there appears to be some exceptions, which we shall presently notice. It is found that "*the separation of any two bodies is attended with the absorption of a quantity of heat equal to that which is evolved in their combination.*" The truth of this proposition has been established by Dr. Woods* and Mr. Joule,† by comparing the heat evolved in the electrolysis of water with that which is developed in a thin metallic wire by a current of the same strength. The current was first made to pass through a vessel containing acidulated water, the quantity of gas evolved in a given time determined, and also the rise of temperature, the strength of the current being at the same time measured by the tangent compass. The electrolytic cell was then removed, and a thin platinum wire introduced between the poles, of such a length as to produce a resistance equal to that of the electrolyte. The quantity of heat evolved in this wire was then determined, and found to exceed that which was previously evolved in the electrolytic cell by a quantity equal to that which would be evolved in the combination of the oxygen and hydrogen eliminated by the current in the previous experiment.

1392. "The same proposition is likewise established by many other chemical phenomena. When zinc dissolves in dilute sulphuric acid, the action may be supposed to consist of three stages, viz., the decomposition of water, the formation of oxide of zinc, and the combination of the oxide of zinc with sulphuric acid, forming ZnO, SO_3. Now,—

	Heat units.
The heat evolved in the oxidation of 1 atom or 32·6 parts of zinc - - - - - =	42,413
The heat evolved in the combination of 1 atom or 40·6 parts of oxide of zinc, with sulphuric acid, in presence of a large quantity of water - - - - - =	10,455
	52,868
Deducting from this the heat evolved in the combination of 1 atom or 1 gramme of hydrogen with oxygen - - - - =	34,462
There remains for the heat evolved in the entire process - - - - - -	18,406

which agrees very nearly with the quantity determined by direct experiment, viz., 18,514 heat units.

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* *Phil. Mag.* [4], ii. 368.

† *Phil. Mag.* [4], iii. 481.

1393. "Again, when metallic oxides are reduced by hydrogen, the heat evolved is not so great as when the same quantity of hydrogen combines with oxygen, because it is diminished by the heat absorbed in the separation of the oxygen and the metal.

1394. "The reduction of oxide of iron by hydrogen takes places without much evolution of heat, because the heat evolved in the combination of 1 gramme of oxygen with hydrogen, viz., 4,308 heat units, is not much greater than that which is evolved when the same quantity of oxygen combines with iron, viz., 4,134 heat units. But the reduction of oxide of copper is attendant with a rise of temperature amounting to incandescence, because the heat evolved in the oxidation of hydrogen greatly exceeds that which is evolved in the oxidation of copper, which is only 2,393 heat units.

1395. "The absorption of heat in decomposition is also demonstrated by the fact that no alteration of temperature takes place in the double decomposition of salts, provided all the products remain in solution; in fact, the heat evolved in the combinations is exactly compensated by the cold produced by the decompositions which take place at the same time; but if a precipitate is formed, heat is evolved, in consequence of the passage of the compound from the liquid to the solid state."*

1396. We will now notice some exceptions to the rule that heat is always absorbed in chemical decomposition. In the decompositions of some of the oxides of chlorine, and of the chloride and iodide of nitrogen, heat is evolved. Heat is also evolved in the decomposition of peroxide of hydrogen, and of gun cotton; and Favre and Silbermann found that when carbon is converted into carbonic acid by burning it in protoxide of nitrogen, more heat is evolved than by its combustion in pure oxygen. Thus its calorific power by combustion in the former gas was found to be 1,115, or 3,078 in excess of 8,080, its calorific power when burned in oxygen; they therefore draw the conclusion that a large amount of heat is evolved in the separation of the protoxide into its elements. They estimate the amount, from the experiment just described, to be 1,158 units for a quantity of the compound which contains 1 gramme of oxygen.

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* Graham's "Chemistry," vol. ii., edited by Watts.

1397. *Calorific intensity.*—We have seen (1287) that thermometers measure, not the *amount* of heat, but its *intensity;* in other words, the temperature; and that these instruments can only be employed to measure temperatures under 600° F. To measure temperatures higher than this, instruments termed pyrometers are employed; but these instruments, owing to their imperfections, are rarely if ever employed in practice.* We are obliged, therefore, to have recourse to the elementary composition of fuel to determine its *pyrometrical heating effect,* or as it is also named, its *calorific intensity.*

1398. The absolute heating power of combustible substances has been determined, we have seen, by observing the amount of heat they respectively communicate to a given amount of water. The pyrometrical heating effect is obtained by the transference of the heat to the combustion products. The difference between the *calorific power* and the *calorific intensity* will perhaps be more clearly seen if we illustrate the difference by examples. The calorific power of carbon is 8,080; in other words, the heat generated during the combustion of 1 *part* of carbon will raise 8,080 parts of water 1° C., or will heat 1 part of water from 0° to 8,080° C., or will raise 3·67 parts of water from 0° C. to $\frac{8080}{3{\cdot}67} = 2202$. Now 3·67 parts of carbonic acid are produced by the combustion of one part of carbon; and if the heat produced by the combustion be transferred to the carbonic acid, and not to water, the temperature of the carbonic acid would be 2,202 if its specific heat were the same as that of water; but this is not the case. The specific heat of carbonic acid is 0·2164, taking water as unity; the temperature of the carbonic acid will consequently be in the inverse ratio, or

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* M. Regnault, in the *Annal de Chimie et de Physique* for 1861, describes a gas thermometer or pyrometer for measuring accurately high temperatures. He states that it requires very little time for determining temperatures by means of it; and that after one observation has been made, the instrument is adapted immediately for recording another. It is therefore capable of measuring the variable temperatures of the same furnace. M. Regnault has proposed to employ it in determining the temperature of the furnaces in the Imperial Porcelain Manufactory at Sèvres.

$\frac{2202}{0{\cdot}2164} = 10175{\cdot}5$; this is the pyrometrical heating power, or calorific intensity of carbon when burnt in *oxygen gas. The calorific intensity of a simple combustible body is obtained by dividing its calorific power by the product of the relative weight of its combustion product into the specific heat of that product.*

1399. In determining the calorific power of hydrogen, the compound (water) produced is in the state of vapour, but becomes condensed; the heat estimated in the calorimeter is therefore the heat of combination plus the latent heat; but in determining the calorific intensity, the latent heat has to be deducted. The calorific power of carbon is 8,080; that of hydrogen, 33,808: but the calorific intensity of carbon is 10173·7; whilst the calorific intensity of hydrogen is only 6777·7. The reason of carbon exceeding hydrogen in calorific intensity, is due to two causes,—1st, the specific heat of aqueous vapour is about twice as great as that of carbonic acid; 2nd, 1 part of hydrogen produces 9 parts of water, whilst 1 part of carbon produces only 3·67 parts of carbonic acid; and to these two causes must, under certain circumstances, be added a third, viz., the latent heat carried off by the steam. We find their calorific intensity in the following manner:—

$$\frac{8080}{3{\cdot}67 \times 0{\cdot}2164} = 10173{\cdot}7 \text{ calorific intensity of carbon in oxygen gas.}$$

$$\frac{33808 - (537 \times 9)}{9 \times 0{\cdot}477} = 6777{\cdot}7 \text{ calorific intensity of hydrogen in oxygen gas.}$$

When the fuel or combustible substance is employed for temperatures higher than 100° C., the water produced by the combustion will escape as steam; the latent heat of the steam will not, under such circumstances, become available; it therefore diminishes the available heating power of the fuel, and must consequently be deducted. The total heat of steam at 100° C. is 637, but this includes the heating of the water from 0° to 100°; as the temperature can never be below 100° C., the actual amount of heat carried off by the steam must be $637 - 100 = 537$.

1400. The calorific power of a substance is the same, whether burnt in pure oxygen or in atmospheric air; but the calorific intensity is much greater when the substance is burnt in oxygen gas than when burnt in atmospheric air, because the nitrogen, which takes no part in the combustion, absorbs a certain amount of heat, and thus lowers the temperature. The calorific intensity of a simple combustible in air is therefore obtained by dividing its calorific power by the *sum* of the products of the relative weight of its combustion product into its specific heat, and the product of the weight of nitrogen (in the air required for the combustion of the substance) into its specific heat. We find, for example, the calorific intensity of 1 part of hydrogen, when burnt in air, in the following way:—As 8 parts of oxygen are contained in 34·63 parts of air, that quantity of air will be required for the combustion of 1 part of hydrogen, and in that quantity of air there is, of course, 26·63 parts of nitrogen. We consequently multiply this quantity of nitrogen by the specific heat of nitrogen, which is 0·244, and add the product to the product obtained by multiplying the weight of the combustion product of hydrogen into the specific heat of that product, and divide the number representing the calorific power of hydrogen, minus the latent heat of steam, by this sum:—

$$\frac{33808 - (537 \times 9)}{9 \times 0{\cdot}475 + 26{\cdot}63 \times 0{\cdot}244} = 2689{\cdot}6$$

EXERCISES.

205. Determine the calorific intensity of 1 part of carbonic oxide when burnt in pure oxygen gas.

206. Determine the calorific intensity of 1 part of carbon when burnt in atmospheric air.*

207. Determine the calorific intensity of 1 part of carbonic oxide when burnt in atmospheric air.

1401. The student will learn, from exercises 206 and 207, that the calorific intensity of carbonic oxide is greater than even that of carbon, when they are burnt in atmospheric air; this may at first appear to him paradoxical, but if he will contrast the calorific intensities of these two substances when they are burnt in oxygen, he will see that it is due to the lesser amount of air the carbonic oxide requires for its combustion. The probable reason why there is not a greater difference between the calorific intensities of carbon and carbonic oxide when they are burnt in oxygen gas is given in par. 1371.

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* The student should contrast the difference between the calorific intensity of carbon and hydrogen, when burnt in oxygen gas, and their difference when burnt in air.

1402. The student will see, from the exercises and examples, that the difference in the calorific intensity of carbon and hydrogen is not so great when those substances are burnt in air as when they are burnt in pure oxygen gas; but even in air the pyrometrical heating power of carbon is greater than that of hydrogen, consequently the greater the quantity of carbon in a fuel the greater the calorific intensity of the fuel.

1403. In substances containing oxygen, it is necessary to deduct from the total quantity of hydrogen the quantity necessary to combine with the oxygen in the substance, and to account, as available for raising the temperature, only the remaining hydrogen with the carbon; the quantity of water which is formed by the combustion of the hydrogen by the oxygen in the fuel, as well as that formed by the combustion of the hydrogen by the oxygen of the air, will require to be evaporated, and will, therefore, diminish the available heat.

EXERCISES.

208. Calculate the calorific intensity of ether (C_4H_5O) in oxygen gas and in atmospheric air.

209. Calculate the calorific intensity of alcohol (C_4H_5O, HO) in oxygen gas and in atmospheric air.

1404. The pyrometrical heating effect of any other kind of combustible or fuel, however numerous its constituents may be, is ascertained in the same way, viz., by finding the absolute heating power in the way already made known, and dividing it by the sum of the specific heat of the products of combustion, multiplied by their total weights, and the product of the weight of nitrogen (in the air required for the combustion of the substance) into its specific heat; the quotient will be the available heat for any particular work when the fuel is burned.

EXERCISES.

210. A caking coal from Northumberland was found to have the following per-centage composition:—

Carbon	80·54
Hydrogen	4·76
Oxygen	14·70
	100·00

Determine its calorific intensity from these numbers.

211. A non-caking coal from South Staffordshire was found to have the following per-centage composition:—

Carbon	78·46
Hydrogen	4·96
Oxygen	16·58
	100·00

Determine its calorific intensity from these numbers.

212. A non-caking coal from Dowlais, South Wales, was found to have the following per-centage composition:—

Carbon	91·64
Hydrogen	4·54
Oxygen	2·64
Nitrogen	1·18
	100·00

Determine its calorific intensity from these numbers.

213. A cannel coal from Tyneside was found to have the following per-centage composition:—

Carbon	87·86
Hydrogen	7·53
Oxygen	2·53
Nitrogen	2·08
	100·00

Determine its calorific intensity from these numbers.

214. An anthracite from South Wales was found to have the following per-centage composition:—

Carbon	94·05
Hydrogen	3·38
Oxygen	2·57
	100·00

Determine its calorific intensity from these numbers.*

1405. It is important to know, not only the calorific power of a given *weight* of any particular fuel, but also the calorific power of a given *volume* of the fuel, say a cubic foot; this is obtained by multiplying the calorific power of a given weight of the fuel, by the weight of a cubic foot.

EXERCISES.

215. Determine the pyrometrical heating power of a cubic foot of each of the coals named in the preceding exercises, taking the sp. gr. of the coal in Exercise 210 to be 1·26; that in Exercises 211, 212 to be 1·28; that in 213 to be 1·32, and that in 214 to be 1·35.

1406. For those who can make use of them, the following formulæ will be found most valuable:—

FORMULÆ FOR THE "CALORIFIC INTENSITY," OR "PYROMETRICAL HEATING EFFECT" OF FUEL (ON THE HYPOTHESIS THAT NO HEAT IS LOST BY RADIATION OR CONDUCTION).

CARBON BURNED *in pure oxygen.*

Let k = *calorific power*, or *absolute heating effect* of carbon.
x = weight of carbon, with reference to any unit.
$\frac{8}{3}x$ = weight of oxygen which combines with the carbon.
s = *specific heat* of carbonic acid.
I = *calorific intensity* of the combustion-products in degrees Centigrade.

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* The ash is omitted from the analyses of the coals given in this set of exercises.

Hence—

(1). $k\,x$ = No. of heat-units produced by burning the carbon;

$I(x + \frac{8}{3}x)\,s$ = No. of heat-units transferred to the combustion-products;

$$\therefore \quad I\,(x + \tfrac{8}{3}x)\,s = k\,x$$

$$\therefore \quad I = \frac{k\,x}{\frac{11}{3}\,x\,s} = \frac{3\,k}{11\,s}$$

CARBON BURNED *in atmospheric air.*

Let s' = specific heat of nitrogen.

Since the weight of nitrogen mechanically mixed with the weight of oxygen requisite to convert the C into $C\,O_2$ is 9 times the weight of the C (approximately), and the nitrogen present tends only to lower the temperature of the $C\,O_2$ produced:—

$$(2). \qquad I\,(\tfrac{11}{3}\,x\,s + 9\,x\,s') = k\,x$$

$$\therefore I = \frac{k\,x}{x\,(\frac{11}{3}s + 9s')} = \frac{3\,k}{11\,s + 27\,s'}$$

CARBON BURNED *in atmospheric air* (*water* being present).

In this case the absolute heating effect will be *diminished* by the quantity of heat which becomes latent by the conversion of the water into steam.

Let a = weight of water present, in the units formerly employed. This will also represent the weight of *steam* produced. (Latent heat of water = 537° C.)

s'' = specific heat of steam.

Hence—

(3). $k\,x - 537\,a$ = No. of heat-units produced by the combustion;

$I(\frac{11}{3}\,x\,s + 9\,x\,s' + a\,s'')$ = No. of heat-units transferred to the products of combustion, including, in this case, *steam;*

$$\therefore I = \frac{k\,x - 537\,a}{x\,(\frac{11}{3}\,s + 9s') + a\,s''}$$

HYDROGEN BURNED *in pure oxygen.*

Let h = weight of hydrogen;

k' = its calorific power.

In this case the water produced ($= 9\,h$) is in the state of vapour, and its *latent heat* must be *deducted*, as before.

Hence—

$$(4).\qquad I \times 9\,h\,s'' = k'\,h - (537 \times 9h)$$

$$\therefore I = \frac{h\,(k' - 4833)}{9\,h\,s''} = \frac{k' - 4833}{9\,s''}$$

HYDROGEN BURNED *in atmospheric air.*

In this case the weight of nitrogen mechanically mixed with the weight of O requisite to convert the H into H O, is 26·63 times the weight of the H.

Hence—

$$(5).\qquad I = \frac{k'\,h - 4833\,h}{9\,h\,s'' + 26{\cdot}63\,h\,s'}, = \frac{k' - 4833}{9\,s'' + 26{\cdot}63\,s'}$$

CARBON AND HYDROGEN BURNED *in pure oxygen.*

$$(6).\qquad I = \frac{k\,x + h\,(k' - 4833)}{\frac{11}{3}\,x\,s + 9\,h\,s''}$$

CARBON AND HYDROGEN BURNED *in atmospheric air.*

In this case the number of heat units absorbed by the nitrogen will be expressed by $I\,(9\,x\,s' + 26{\cdot}63\,h\,s')$.

Hence—

$$(7).\qquad I = \frac{k\,x + h\,(k' - 4833)}{\frac{11}{3}\,x\,s + 9\,h\,s'' + (9\,x\,s' + 26{\cdot}63\,h\,s')}$$

$$= \frac{k\,x + h\,(k' - 4833)}{x\,(\frac{11}{3}s + 9\,s') + h\,(26{\cdot}63\,s' + 9\,s'')}$$

CARBON, HYDROGEN, AND OXYGEN BURNED *in atmospheric air,*

the oxygen present not being in a greater ratio than would be requisite to convert the hydrogen into water.

In this case the amount of hydrogen available for raising the temperature will be represented by $h - h'$, (h' being taken to represent the amount of hydrogen which combines with the oxygen present in the fuel).

Formula (7) will have to be modified thus:—

$$(8).\quad I = \frac{k\,x + k'\,(h - h') - 4833\,h}{x\,(\tfrac{11}{3}\,s + 9\,s') + h\,(26{\cdot}63\,s' + 9\,s'')}$$

If a solid body which is unaltered by the combustion be present, such as ashes in coal, its weight multiplied by its specific heat must be added to the divisor. The quantity of heat lost by the presence of ash in coal is so insignificant that the results are but very slightly affected if the ash be left out of the calculation.

If *ash* be among the products of combustion, let z = its weight, and σ = its specific heat:—

Then formula (8) becomes,—

$$(9).\quad I = \frac{k\,x + k'\,(h - h') - 4833\,h}{x\,(\tfrac{11}{3}\,s + 9\,s') + h\,(26{\cdot}63\,s' + 9\,s'') + z\,\sigma}$$

If, in the combustion of the charcoal, some *carbonic oxide* is formed, the temperature will be *diminished*.

Let x' = weight of carbon converted into C O.
$\tfrac{4}{3}\,x'$ will be the weight of the O combined with x' to form C O.
k'' = calorific power of C O.
s''' = specific heat of C O.

Hence—

$$(10).\quad I = \frac{k\,x + k''\,x' + k'\,h - 4833\,h}{\tfrac{11}{3}\,x\,s + (x' + \tfrac{4}{3}\,x')\,s''' + 9\,h\,s'' + (9x\,s' + 26{\cdot}63\,h\,s')}$$

$$= \frac{3\{k\,x + k''\,x' + h\,(k' - 4833)\}}{x\,(11\,s + 27\,s') + 7\,x'\,s''' + h\,(79{\cdot}89\,s' + 9\,s'')}$$ [*]

1407. *Thomson's apparatus for determining the absolute heating power of fuel.*—Mr. Lewis Thomson has invented a very convenient apparatus for determining the absolute heating power of fuel. The apparatus has been constructed on the following principles:[†]—First, that the latent heat of steam is equal to 967° F.; and, secondly, that fuel, burned in pure oxygen, evolves the same amount of heat as when perfectly burned in atmospheric air. The experiment is conducted in the following way:—Thirty grains of the finely-powdered sample of coal, or other fuel, are very intimately mixed with from 300 to 360 grains of a mixture composed of three parts of chlorate of potash to one of nitrate of potash. The mixed mass is then introduced into a copper cylinder column, which forms the furnace. This is then placed on a brass base, and a hole is made in the mixture to receive a fusee (a little cotton wick which has been dipped in nitre, and which serves as a slow match), about half an inch in depth, which is fixed by pressing the mixture around it. A copper cylinder, with a long copper tube fitted with a stop-cock, is called the enclosure. The copper cylinder is perforated with a number of small holes to allow the gases produced by the combustion to pass through the water, and thus give up their heat to it. The copper cylinder is fitted over the furnace, and when the furnace and cylinder, thus joined, are introduced into water, the water is excluded or admitted to the furnace according as the stop-cock is shut or opened. A glass cylinder, filled with water up to a certain mark, holds 29,010 grains. The temperature of the water is determined by a very delicate thermometer. It ought to be about 60° F. at the commencement of each experiment. The temperature of the water having been determined, the fusee is lighted, and the enclosure, with its stop-cock closed, is fixed over the furnace. The whole apparatus is then submerged in the water contained in the glass cylinder. A minute or so after the immersion, the wick burns down to the mixture, its combustion then commences, and when it ceases, the stop-cock is opened, and the apparatus (furnace and enclosure) moved gently up and down in the water, which causes the fluid within and without the enclosure to acquire the same temperature. The increased temperature of the water is then determined by means of the thermometer. The number of degrees to which the water has been heated, represents the quantity of water which would be converted into steam from a temperature of 212° F. If, for example, the temperature of the water has been raised 10°, we learn that the sample of fuel under examination would be capable of converting ten times its weight of water into steam, since every grain of the fuel has been burnt in the midst of 967 grains of water; and if the latent heat of steam be taken at 967° F., then if 967 grains of water be raised 10°, sufficient heat has been generated to boil off 10 grains of water from 212° F.: substituting the word pounds for grains, we have at once the evaporative value of the coal.

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[*] I am indebted to my friend, Charles W. Bateman, LL.D. (Ex. Schol. Trin. Coll., Dublin), for these formulæ.

[†] For a further description of the apparatus, and for an illustration, the student is referred to a little tract entitled, "The Analysis of Gas, for Practical Men," published by Alexander Wright, of 55, Millbank Street, Westminster, where also may be purchased Mr. Thompson's apparatus.

1408. As part of the heat generated by the coal is absorbed by the instrument, this per-centage must be added to every calorific result obtained.*

1409. *On the burning of fuel.*—Owing to several causes,

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* "The absolute thermal effects of different fuels,—different combustibles,—are represented in this table, and you will there see the great pre-eminence of hydrogen in this respect. Taking the absolute thermal effect of carbon as unity, the same weight of hydrogen produces in its combustion nearly 4½ times the heat of the carbon; and olefiant gas 1½ times, and so on. Here is the table:—

Absolute thermal effect of combustibles.

Hydrogen - - -	4·46	Alcohol - - - -	0·86
Olefiant gas - - -	1·52	Good coal - - -	0·77
Olive oil - - - -	1·22	Dry wood - - -	0·46
Ether - - - -	1·02	Air-dry wood - - -	0·45
Carbon - - - -	1·00	Peat - - - -	0·36
Charcoal - - - -	0·96		

The absolute thermal effect, ascertained by experiments of this kind, of different kinds of fuel in ordinary use, especially of the two kinds of fuel generally used for heating purposes, in contradistinction to gas, is shown in this table.

"Quantity and cost of gaseous and solid fuel required to evaporate 1,000 lbs. of water from 212°:—

1,833 cubic feet of coal gas cost,	at 4s. per 1,000 cubic feet	7s. 4d.
2,874 „ water gas	at 2s. „ „	5s. 9d.
125 lbs. coke - - -	at 20s. per ton - -	1s. 1d.
112 lbs. coal - - -	at 20s. „ - -	1s. 0d.

1,833 cubic feet of coal gas, at 4s. per thousand, are required to evaporate 1,000 lbs. of water from 212°. To do this amount of work, therefore, you are required to employ a quantity of gas which costs 7s. 4d. If, in the place of coal gas, you use gas which is produced from water by charcoal,—a mixture of hydrogen and carbonic oxide chiefly,—2,874 cubic feet are necessary, which will cost the sum of 5s. 9d. for that amount of heating power: 125lbs. of coke will do precisely the same amount of work—will heat exactly the same quantity of water to the same temperature—for 1s. 1d., or 112 lbs. of coal will do the same for 1s. I have put this diagram before you to show at a glance the great difference there is between these kinds of fuel. You see that coal and coke produce a much greater amount of heat at a less cost than gas, although gas has been proposed for heating purposes; and no doubt there are great facilities for the use of gas which may contribute, to some extent, to counterbalance the great discrepancy in its cost."—*Lectures delivered by Dr. Frankland before the Royal Institution. See "Chemical News,"* vol. iii., 1861.

the total theoretical heating power of fuel is never obtained in practice. 1st. The fuel is scarcely ever completely consumed, a part escapes combustion by passing off in the form of combustible gases and smoke, and another part remains mixed up with the ash. 2nd. There is loss of heat from radiation, and also from *conduction*; the loss by conduction not only occurs through the matter forming the furnace, but also by means of the gaseous current which is constantly flowing through the *incandescent* fuel. In calculating the calorific intensity, the *theoretical amount of air required for the combustion of the fuel is employed*, but in practice this is, generally speaking, never accomplished, for it requires, in order to approach theory, the most favourable circumstances,—such as properly arranged furnaces, the adjustment of the fuel, and draught of air passing through the fire; this latter requires skill and constant attention on the part of the fireman; generally too much air is allowed to pass through the fire, which increases the loss of heat; and the loss from this cause is greater than is generally supposed.

1410. "In calculating the theoretical temperature it is presumed that the oxygen of the air is in contact with every particle of the fuel during ignition. Could the same condition be insured in the furnace, it is evident that the great desideratum required in combustion would be attained; no escape of combustible gas could then ensue, nor of the carbonaceous particles which give to the gases passing up the chimney the character of smoke; and the greatest possible heat arising from the burning of the substance in air would be developed. Indeed, nothing would be wanting to extract from the fuel the benefit of its total theoretical heating power, but such an arrangement of the furnace as would perfectly utilize the caloric so produced. No one, however, who has any experience as to the manner in which the fire is managed in the ordinary kinds of furnaces, will hesitate to assert that the above conditions are never supplied."*

1411. The time required for the combustion of the fuel, and, consequently, for the evolution of heat, depends upon its state of division and aggregation, and also upon its chemical composition. If the fuel be thrown on the fire in large pieces, it burns slowly, and a large proportion of the heat generated is absorbed. If it be wood that is employed, and instead of being burnt in the form of large logs, it be first divided into shavings, the combustion will be so rapid that a large proportion of the heat will, for all useful purposes, be lost. This arises from the greater facility with which the air comes in contact with it, when in the form of shavings. If, however, the fragments are still further reduced in size, the smallness of the particles, and the close contact existing between them, excludes the entrance of the necessary supply; and for this reason it is extremely difficult to obtain any available heat, either from sawdust, or very finely-divided coal. But in determining the value of a fuel, not only must the state of division, but also the state of aggregation be taken into account; thus, "particular qualities of charcoal, coke, and anthracite may have the same calorific power, and yet differ remarkably in their manner of burning. Of the three, charcoal, being very light and porous, ignites most easily, and in a given volume contains the least combustible matter; and accordingly, under the same conditions, it is most quickly consumed. Coke also contains less combustible matter in a given volume, and, except when prepared at high temperatures, is more easily ignited than anthracite. The practical effect of these differences in the manner of burning will be well understood by experimenting on these three kinds of fuel in a common casting furnace about one foot square and from two to three feet deep. If an attempt is made to heat a large crucible in such a furnace by means of anthracite, it will be found that the bottom becomes heated to whiteness before the top is hardly red-hot; whereas, by the use of coke, the temperature is not so excessive at the bottom, but is more equally diffused through the furnace. The effect of anthracite as a fuel, is the rapid production of an intense heat confined to a space not extending beyond a few inches above the bars."*

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* Muspratt's "Applied Chemistry."

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* It is obvious that, on this account, anthracite is not adapted as a fuel for ordinary steam-boiler furnaces; but by the following simple contrivance, it may be advantageously employed in these furnaces. The ash-pit is kept filled with water, and deep, fish-bellied bars are used, of which the lowest parts nearly, if they do not actually, touch the water. Steam is necessarily evolved from the surface of the water, and enters the fire place along with the atmospheric air which sustains combustion. On passing through the

1412. The student will have learned from the exercises that the more carbonaceous the fuel, the greater its calorific intensity; hence charcoal, coke, and the highly carbonaceous coals of South Wales, are well adapted for purposes where a high localized temperature is required, as in the smelting of iron; but for steam purposes, where a more diffused heat is required, and where, especially, the steam is required at intervals, a coal containing more hydrogen will be better adapted for the purpose.

CHAPTER XIV.

DIFFUSION OF LIQUIDS—DIALYSIS—OSMOSE.

Introduction, 1413. *Characters of liquid diffusion*, 1423. *Diffusion of various salts and other substances*, 1428. *Diffusibility of acids*, 1435. *Diffusion of mixed salts*, 1447. *Separation of salts of different bases by diffusion*, 1448. *Decomposition of salts by diffusion*, 1449. *Diffusion of double salts*, 1456. *Diffusion of one salt into the solution of another salt*, 1461. *Diffusion of salts of potash and ammonia*, 1467. *Crystalloid and colloid substances*, 1470. *Effect of temperature on diffusion*, 1483. *Diffusion of crystalloids through colloids*. 1484. *Dialysis*, 1489. *Distinction between crystalloids and colloids*, 1496. *Application of dialysis*, 1507. *Osmose*, 1527.

1413. In this chapter I have endeavoured to place before the student a full and accurate abstract of the researches of Mr. Graham on liquid diffusion; this ab-

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incandescent anthracite, it is decomposed, with the formation of the combustible gases, carbonic oxide and hydrogen, which are afterwards burned under the boiler at a distance from the fire, by the admission of a suitable supply of atmospheric air from without. The decomposition of the steam causes a considerable diminution of temperature within the fire place, but there is no permanent loss of heat, as, on the subsequent burning of the combustible gases derived from the steam, the heat absorbed in the first instance is again given out and economised; there is, so to speak, only a transference of heat from the fire place to a distance. The bars do not become sufficiently heated to burn rapidly away. The fire place should be enclosed above by a fire-brick arch, as no part of the boiler should be unprotected above the solid fuel."—*Dr. Percy's "Metallurgy."*

stract I have taken from the various memoirs* which Mr. Graham has written upon this subject; I have merely altered the arrangement and condensed the reports.

1414. Any saline or other soluble substance, once liquefied and in a state of solution, is evidently spread or diffused uniformly through the mass of the solvent by a spontaneous process. The cold produced on diluting certain saline solutions, Gay Lussac explains by assuming that liquid diffusion resembles gaseous diffusion, and that the molecules of the salt expand into the water like a compressed gas into additional space. He also regards the phenomena of solubility as radically different from those of chemical affinity, and as the result of an attraction which is of a physical or mechanical kind. The characters, indeed, of these two attractions are strongly contrasted. Chemical combination is uniformly attended with the evolution of heat, while solution is marked with equal constancy by the production of cold. The substances which combine chemically are the dissimilar, while the soluble substance and its solvent are the like, or analogous in composition and properties.

1415. In the consideration of solubility, attention is generally engrossed entirely by the quantity of salt dissolved. *But it is necessary to apprehend clearly another character of solution, namely, the degree of force with which the salt is held in solution, or the intensity of the solvent attraction, quite irrespective of quantity dissolved.* In the two solid crystalline hydrates, pyrophosphate of soda and sulphate of soda, we see the same ten equivalents of water associated with both salts, but obviously united with unequal degrees of force, the one hydrate being persistent in dry air, and the other highly efflorescent. So, also, in the solutions of two salts which are equally soluble in point of quantity, the intensity of the attraction between the salt and the water may be very different, as exemplified in the large but feeble solubility in water of such bodies as iodide of starch, or the sulphindylate of potash, compared with the solubility of hydrochloric acid, or of the acetate of potash, which last two substances are capable of precipitating the two former, by displacing them in solution. Witness, also, the unequal action of animal charcoal in withdrawing different salts from solution, although the salts are equally soluble; and the unequal effect upon the boiling point of water produced by dissolving in it the same weight of various salts. Besides being said to be *small* or *great*, the solubility has also therefore to be described as *weak* or *strong*. It becomes a question how far these gradations of intensity are dependent upon unequal diffusibility; whether, indeed, rapidity of diffusion is not a measure of the force in question.

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* "On the Diffusion of Liquids."—*Philosophical Transactions*, 1850.
"Supplementary Observations on the Diffusion of Liquids."—*Phil. Trans.* 1850.
"On the Application of Liquid Diffusion to produce Decompositions."—*Quarterly Journal, Chemical Society*, vol. iii., 1851.
"On Osmotic Force."—*Phil. Trans.*, 1854.
"Liquid Diffusion applied to Analysis."—*Phil. Trans.*, 1861.

1416. As liquid diffusion has been compared to gaseous diffusion, it is necessary to notice the views which may be taken of the physical agency by which gaseous diffusion is effected; two views may be taken, each equally tenable, as each is entirely sufficient to explain the phenomena.

1417. On one theory, that of Dalton, the diffusibility of a gas is referred immediately to its elasticity. The same spring, or self-repulsion of its particles, which sends a gas into a vacuum, is supposed to propel it through and among the particles of a different gas.

1418. The existence of an attraction of the particles of one gas for the particles of all other gases is assumed in the other theory. This attraction does not occasion any diminution of volume of gases on mixing, because it is an attraction residing on the surfaces of the gaseous molecules. It is of the same intensity for all gases, hence its effect in bringing about intermixture is dependent upon the weight of the molecules of the gases to be moved by it, and the velocity of diffusion of a gas comes to have the same relation to its density on this hypothesis as upon the other. This assumption of surface attraction of gaseous molecules reminds one of the surface attraction of liquids, which is found necessary to account for the elevation of liquids in tubes, and other phenomena of capillary attraction.

1419. We are indebted to Mr. Graham for a minute investigation of the phenomena of liquid diffusion. The apparatus he employed in these researches consisted of a set of phials of nearly equal capacity, all cast in the same mould, and further adjusted by grinding to a uniform size of aperture. The dimensions for a phial (Fig. 35) were 3·8 inches in height, with a neck 0·5 inch in depth; aperture, 1·25 inch in diameter; and capacity to base of the neck, 2,080 grs. of water, or between 4 and 5 ozs. For each phial a plain glass jar was also provided, 4 inches in diameter, and 7 inches in depth. The method of observing the diffusion of a salt will be best explained by an example.

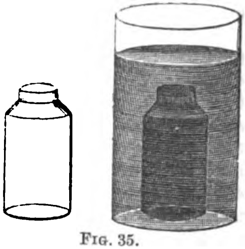

FIG. 35.

1420. It was necessary, Mr. Graham remarks, to observe the spontaneous diffusion into pure water of several salts, already dissolved in 100 times their weight of water. The phial was filled with such a solution of sal ammoniac, for instance, to the base of the neck, or, more correctly, to a distance of exactly 0·5 inch from the ground surface of the lip. The neck of the phial was then filled up with distilled water, a light float being placed on the surface of the solution, and care taken to avoid agitation after the phial had been placed within the jar. The latter was then filled up with distilled water, so as to cover the open phial to the depth of an inch, which required about 20 ounces of water. The saline liquid in the "solution-phial" is thus allowed to communicate freely with the water of the "water jar," which is about five times its volume. The water of the latter forms an atmosphere into which salts spread or diffuse, escaping from the solution phial with different degrees of velocity. The phial and jar together form the "diffusion cell." The diffusion is interrupted by placing a small plate of ground glass upon the mouth of the phial, and raising the latter out of the jar. The amount of salt diffused, or the "diffusion product," is learned by evaporating the water of the jar to dryness, or, in the case of chlorides, by precipitating with nitrate of silver; in the case of acids the quantities diffused were determined by neutralizing the diffusion product with a normal alkaline solution. The diffusion, as a rule, was allowed to proceed for a period of seven days, and the temperature of the room in which the experiments were made did not vary more than one degree on either side 50° F.

1421. The 1 per cent. solution of sal ammoniac, in the solution phial, would contain 20·8 grains of salt. Of this quantity of salt, 3·49 grs. were found to diffuse out into the water jar in the time mentioned in one experiment, and 3·36 grs. in another experiment. The mean of these two diffusion products is 3·42 grs., which is therefore the quantity of chloride of ammonium diffused out of the solution phial, containing 1 per cent. solution of that salt, in a period of seven days.

1422. The diffusion of a 1 per cent. solution of chloride of sodium in similar circumstances gave, in eight cells, the following products :—3·02, 2·83, 2·86, 2·68, 2·74, 2·70, 2·80, and 2·94 grs., of which the mean is 2·85 grs. These results for the chlorides of ammonium and sodium approach to the theoretical ratio of 1·4142 to 1·7320; that is, of the square root of 2 to the square root of 3.

1423. *Characters of liquid diffusion.*—The characters of liquid diffusion were first examined by Mr. Graham in detail in the case of chloride of sodium, and the first question he proceeded to answer experimentally was this, —Do different proportions of chloride of sodium in solution give corresponding amounts of diffusion? Four different solutions of common salt in water were prepared, containing respectively 1, 2, 3, and 4 parts of salt to 100 parts of water. In eight days' time the quantities diffused were—in the first solution, 2·78 grs.; in the second, 5·54 grs., or just double the amount; in the third, 8·37 grs., or three times the quantity; and in the fourth, 11·11 grs., or almost exactly four times the amount diffused from the first solution. The quantities diffused appear, therefore, to be closely in proportion (for this salt) to the quantity of salt in the diffusing solution.

1424. The next question which Mr. Graham proceeded to answer experimentally was this,—Is the quantity of salt diffused affected by the temperature? The diffusion of similar solutions of chloride of sodium was repeated at two new temperatures,—39°·6 and 67°,—the one above and the other below the preceding temperature (52°·5.)

Proportion of salt to 100 water.	Diffusion product.	
	In grains.	Ratio.
1, at 39°·6 - - -	2·63	1·
2, " " - - -	5·27	2·
3, " " - - -	7·69	2·92
4, " " - - -	10·00	3·80
1, at 67° - - -	3·50	1·
2, " " - - -	6·89	1·97
3, " " - - -	9·90	2·83
4, " " - - -	13·60	3·89

The proportionality in the diffusion is still well preserved at the different temperatures. The deviations are indeed little, if at all, greater than might be occasioned by errors of observation. The ratio of diffusion, for instance, from the solutions containing 4 parts of salt, is 3·80 and 3·89 for the two temperatures, which numbers fall little sort of 4. The diffusion manifestly increases with the temperature, and, as far as can be determined by three observations, in direct proportion to the temperature. The diffusion product from the 4 per cent. solution increases from 10 grains to 13·6, with a rise of temperature of 27°·4, or rather more than one-third. Supposing the same progression continued, the diffusibility of chloride of sodium would be doubled by a rise of 84 or 85 degrees.

1425. The progress of the diffusion of chloride of sodium in such experiments as the preceding ones, was further studied by intercepting the operation after it had proceeded for different periods of 2, 4, 6, and 8 days. The strength of the solution employed was 4 parts of salt to 100 of water. In 2 days, temp. 63°·7, the salt diffused was 3·95 grains. In 4 days, temp. 63°·7, the salt diffused was 6·95 grains. In 6 days, temp. 63°·8, the salt diffused was 9·86 grains. In 8 days, temp. 64°, the salt diffused was 13·12 grains.

1426. The proportion diffused in the first period of two days is given directly in the first experiment. The proper diffusion for each of the three latter periods of two days is obtained, of course, by deducting from the result of each period the result of the period which precedes it:—

Diffused in 1st two days	-	- 3·95 grains.
„ „ 2nd „ „	-	- 3·00 „
„ „ 3rd „ „	-	- 2·91 „
„ „ 4th „ „	-	- 3·26 „

The diffusion appears to proceed pretty uniformly, if the amount diffused in the first period of two days be excepted. Each of the phials contained at first about 108 grains of salt, of which the maximum quantity diffused is 13·12 grains in 8 days, or $\frac{1}{8{\cdot}24}$ of whole salt. Still the diffusion must necessarily follow a diminishing progression, which would be brought out by continuing the process for longer time, and appear at the earliest period in the salt of most rapid diffusion.

1427. All the experiments which follow being made, like the preceding, on comparatively large volumes of solution in the phial, and for equally short periods of seven or eight days, may be looked upon as exhibiting pretty accurately the initial diffusion of such solutions, the influence of the diminishing progression being still small. The volume of water in the water jar is also relatively so large, that the experiment approaches to the condition of diffusion into an unlimited atmosphere.

1428. *Diffusion of various salts, and other substances.*

TABLE I.—*Diffusion of solutions of density* 1·200, *temp.* 66° *F., for* 27 *days.*

	Placed in solution cell.		Found in water jar.	
			Diffusion product.	
	Proportion of anhydrous salt, or of acid protohydrate, to 100 of water.	Boiling point.	In grains.	Ratio.
Chloride of sodium	34·21	225°·5	269·80	100
Nitric acid	37·93	227	581·20	215·42
Sulphuric acid	29·03	223	455·10	168·68
Chloride of potassium (density 1·178)	34·86	221	320·30	118·71
Bisulphate of potash	31·85	216	319·00	118·23
Nitrate of soda	32·42	220	260·20	96·44
Sulphate of magnesia	22·38	214	95·87	35·53
Sulphate of copper	21·56	213·5	77·47	28·71

1429. This table of experiments shows that the diffusion from solutions of the same density is not equal, but highly variable, ranging from 1 to 0·133. The results, also, favour the existence of a relation between large or rapid diffusibility and a high boiling point. The latter property may be taken to indicate of itself a high degree of attraction between the salt and water.

TABLE II.—*Diffusion of solutions of* 20 *salt to* 100 *water, at* 60°·5, *for* 8 *days.*

Name of substance.	Density of solution at 60°.	Anhydrous salt diffused, in grs.
Chloride of sodium	1·1265	58·68
Sulphate of magnesia	1·185	27·42
Nitrate of soda	1·120	51·56
Sulphate of water	1·108	69·32
Crystallized cane sugar	1·070	26·74
Fused cane sugar	1·066	26·21
Starch sugar (glucose)	1·061	26·94
Treacle of cane sugar	1·069	32·55
Gum arabic	1·060	13·24
Albumen	1·053	3·08

1430. We learn, from this table of experimental facts, that the diffusion of cane and starch sugar is sensibly equal, and double that of gum arabic. On the other hand, the sugars have less than half the diffusibility of chloride of sodium. It is remarkable that the specifically lightest and densest solutions, those of the sugars and of sulphate of magnesia, approach each other closely in diffusibility. On comparing together, however, two substances of similar constitution, such as the two salts, chloride of sodium and sulphate of magnesia, that salt appears to be the least diffusive of which the solution is densest.

1431. But the most remarkable result is the diffusion of albumen, which is low out of all proportion when compared with saline bodies. The solution employed was the albumen of egg, without dilution, but strained through calico, and deprived of all vesicular matter. As this liquid, with a density of 1·041, contained only 14·69 parts of dry matter to 100 of water, the proportion diffused is increased in the table to that for 20 parts, to correspond with the other substances. In its natural alkaline state the albumen is least diffusive, but when neutralized by acetic acid, a slight precipitation takes place, and the liquid filters more easily: the albumen is now sensibly more diffusive than before. Chloride of sodium appears 20 times more diffusible than albumen in the table, but the disparity is really greater, for nearly one-half of the matter which diffused consisted of inorganic salts. Indeed, the experiment appears to promise a delicate method of proximate analysis peculiarly adapted for animal fluids. The value of this low diffusibility in retaining the serous or albuminous fluids within the blood-vessels at once suggests itself. An examination of the inorganic salts proved that salts of potash diffuse out more freely from albumen than salts of soda.

1432. It was also ascertained that albumen does not impair the diffusion of salts dissolved together with it in the same solution, although the liquid retains its viscosity. Three other substances, added separately, in the proportion of 5 parts to 100 of undiluted solution of egg albumen, were found to diffuse out quite as freely from that liquid as they did from an equal volume of pure water; these were chloride of sodium, urea, and sugar. Urea proved to be a highly diffusible substance; it nearly coincided in rate with chloride of sodium. Further on we shall see to what valuable discoveries this apparently insignificant fact of the low diffusibility of albumen led in the hands of Graham.

1433. Table III. records the diffusion of a series of salts at two different temperatures. Each of the saline solutions contained 1 of salt to 10 of water; this smaller proportion of salt admits of the comparison of a greater variety of salts.

TABLE III.—*Diffusion of solutions of* 10 *salt to* 100 *water, for* 8 *days.*

	Density of solution at 60° F.	Anhydrous salt diffused, in grains.	
		At 37°·5 F.	At 59°·5 F.
Chloride of sodium -	1·0668	22·47	32·25
Nitrate of soda - -	1·0622	22·79	30·7
Chloride of potassium -	1·0596	...	40·15
Chloride of ammonium -	1·0280	31·14	40·20
Nitrate of potash - -	1·0589	28·70	35·55
Nitrate of ammonia -	1·0382	29·19	35·30
Iodide of potassium -	1·0673	28·10	37·0
Chloride of barium -	1·0858	21·42	27·0
Sulphate of water -	1·0576	29·85	36·85
Sulphate of magnesia -	1·0965	13·07	15·45
Sulphate of zinc - -	1·0984	12·60	15·80

1434. The near equality of the quantities diffused of certain isomorphous salts is striking at both temperatures. Chloride of potassium and chloride of ammonium give 40·15 and 40·20 grs. respectively at 59°·5 F.; nitrate of potash and nitrate of ammonia, 35·55 and 35·3 grs. respectively at 59°·5 F., and 28·7 and 29·19 grs. at 37°·5 F.; sulphate of magnesia and sulphate of zinc, 15·45 and 15·8 grs. at 59°·5 F., with 13·07 and 12·60 grs. at 37°·5 F. The relation observed is the more remarkable that it is that of *equal weights* of the salts diffused, and not of *atomically equivalent weights.* In the salts of ammonia and potash this equality of diffusion is exhibited also, notwithstanding considerable differences in density between their solutions, the density of the solution of chloride of ammonium, for instance, being 1·0280, and that of chloride of potassium 1·0596. It may have some relation, however, but not a simple one, to the density of the solutions; sulphate of magnesia, of which the solution is most dense, being most slowly diffusive, and salts of soda being slower, as they are generally denser in solution, than the corresponding salts of potash. Nor does it depend upon equal solubility, for in none of the pairs is there any approach to equality in that respect.

TABLE IV.—*Diffusion of acid solutions* (4 *acid to* 100 *water*), *at* 59°·3 *F.*

Name of acid.	Density of solution at 60°.	Anhydrous acid diffused, in grs.
Nitric acid	1·0243	28·7
Hydrochloric acid	1·0225	34·1
Sulphuric acid	1·0317	18·48
Acetic acid	1·0094	18·16
Oxalic acid	1·0235	12·38
Arsenic acid	1·0320	12·16
Tartaric acid	1·0194	9·79
Phosphoric acid	1·0248	9·09
Chloride of sodium	1·0285	12·32

1435. The experimental facts recorded in this table show that considerable latitude exists in the diffusibility of the different acids. To make the result for nitric acid comparable with that for hydrochloric acid, the former should be increased in the proportion of 54 to 63; that is, estimated as nitrate of water. This calculation gives 33·5 grs. of nitrate of water diffused, which approaches closely to 34·1 grs., the quantity of hydrochloric acid. Sulphuric and acetic acid appear to diffuse equally. The phosphoric acid employed was converted into the tribasic state before experimenting with it; this precaution was not taken with the arsenic acid. These two acids do not exhibit the equality of diffusion anticipated from their recognised isomorphism; but Mr. Graham observes, "It is to be stated that the acidimetrical method of analysis followed is not so properly applicable to these two acids as it is to all the others."

1436. In the following table of experiments the substances were still diffused from weak solutions, that is, from solutions containing from 1 to 8 per cent. of the substance; but now a measure of the solution, equal to 100 grs. of water, was made to contain 1 gr. of the substance, to form what is called the 1 per cent. solution, instead of 1 gr. of the substance being added to 100 grs. of water, as in the preceding experiments, without reference to the condensation which generally occurs; and the quantity diffused is for two cells.

TABLE V.—*Diffusion of saline, acid, &c., solutions.*

Substance.	Per cent.	Days.	Degrees Fahr.	Diffusate.
Hydrochloric acid	1	5	51	7·41
	2	5	51	15·04
	2	5	59·7	16·55
	4	5	51	30·72
	8	5	51	67·68
Hydriodic acid	2	5	51	15·11
Hydrobromic acid	2	5	59·7	16·58
Bromine	0·864	10	60·1	5·84
Hydrocyanic acid	1·766	5	64·2	11·68
Nitric acid (HO, NO_5)	1	5	51·2	6·99
	2	5	51·2	14·74
	4	5	51·2	28·76
	8	5	51·2	57·92
Sulphuric acid (HO, SO_3)	1	10	49·7	8·69
	2	10	49·7	16·91
	4	10	49·7	33·89
	8	10	49·7	68·96
Chromic acid	1·762	10	67·3	19·78
Acetic acid ($HO, C_4H_3O_3$)	2	10	48·8	11·31
	4	10	48·8	22·02
	8	10	48·8	41·80
Sulphurous acid	1	10	68·1	8·09
	2	10	68·1	16·96
	4	10	68·1	33·00
	8	10	68·1	66·38

TABLE V.—*continued.*

Substance.	Per cent.	Days.	Degrees Fahr.	Diffusate.
Ammonia	1	4·04	63·4	4·93
	2	4·04	63·4	9·59
	4	4·04	63·4	19·72
	8	4·04	63·4	41·22
Alcohol	2	10	48·7	8·62
	4	10	48·7	16·12
	8	10	48·7	35·50
Nitrate of baryta	1	11·43	64·1	7·72
	2	11·43	64·1	15·04
	4	11·43	64·1	29·60
	8	11·43	64·1	54·50
Nitrate of strontia	1	11·43	51·5	6·79
Nitrate of lime	1	11·43	64·1	7·66
	2	11·43	64·1	15·01
	4	11·43	64·1	29·04
	8	11·43	64·1	55·10
Acetate of baryta	1	16·17	53·5	7·50
Acetate of lead	1	16·17	53·1	7·84
Chloride of barium	1	8·57	63	6·32
	2	8·57	63	12·07
	4	8·57	63	23·96
	8	8·57	63	45·92
Chloride of strontium	1	8·57	63	6·09
	2	8·57	63	11·66
	4	8·57	63	23·56
	8	8·57	63	44·46
Chloride of calcium	1	11·43	63·8	7·92
	2	11·43	63·8	15·35
	4	11·43	63·8	30·78
	8	11·43	63·8	61·56
	1	11·43	50·8	6·51
Chloride of manganese	1	11·43	50·8	6·63
Nitrate of magnesia	1	11·43	50·8	6·49
Nitrate of copper	1	11·43	50·8	6·44
Chloride of zinc	1	11·43	50·8	6·29
Chloride of magnesium	1	11·43	50·8	6·17
Cupric chloride	1	11·43	50·8	6·06
Ferrous chloride	1	11·43	53·5	6·30

TABLE V.—*continued.*

Substance.	Per cent.	Days.	Degrees Fahr.	Diffu-sate.
Sulphate of magnesia	1	16·17	65·4	7·31
	2	16·17	65·4	12·79
	4	16·17	65·4	23·46
	8	16·17	65·4	42·82
	8	16·17	62·8	42·66
	16	16·17	62·8	75·06
	24	16·17	62·8	102·04
Sulphate of zinc	1	16·17	65·4	6·67
	2	16·17	65·4	12·22
	4	16·17	65·4	23·12
	8	16·17	65·4	42·26
	8	16·17	62·8	39·62
	16	16·17	62·8	74·40
	24	16·17	62·8	101·42
Sulphate of alumina	1	16·17	65·4	5·48
	2	16·17	65·4	10·21
	4	16·17	65·4	19·28
	8	16·17	65·4	33·52
Nitrate of silver	2	7	63·4	13·61
	4	7	63·4	26·34
	8	7	63·4	51·88
Nitrate of soda	2	7	63·4	12·35
	4	7	63·4	23·56
	8	7	63·4	47·74
Chloride of sodium	1	7	63·4	6·32
	2	7	63·4	12·37
	4	7	63·4	24·96
	8	7	63·4	48·44
Iodide of sodium	2	7	59·8	12·18
Bromide of sodium	2	7	59·8	11·93
Chloride of potassium	2	5·716	59·8	12·24
Bromide of potassium	2	5·716	59·8	12·46
Iodide of potassium	2	5·716	59·8	12·51
Chloride of ammonia	1	5·716	53	5·99
Bicarbonate of potash	1	8·08	68·2	7·23
	2	8·08	68·2	14·05
	4	8·08	68·2	26·72
	8	8·08	68·2	52·01

TABLE V.—*continued.*

Substance.	Per cent.	Days.	Degrees Fahr.	Diffusate.
Bicarbonate of ammonia -	1	8·08	68·2	6·91
	2	8·08	68·2	13·65
	4	8·08	68·2	27·00
	8	8·08	68·2	50·10
Bicarbonate of soda - -	1	9·87	68·2	7·31
	2	9·87	68·2	13·81
	4	9·87	68·2	26·70
	8	9·87	68·2	52·38
Hydrochlorate of morphine -	2	11·43	64·1	11·60
Hydrochlorate of strychnine -	2	11·43	64·1	11·49

1437. Hydrochloric acid belongs to the most diffusive class of substances known; its diffusibility increases with its concentration; most other substances, on the other hand, lose proportionally in diffusibility as their solutions are concentrated.

1438. The experimental facts recorded in the table indicate a similarity of diffusion between hydriodic, hydrobromic, and hydrochloric acids. Graham remarks that these acids do not exhibit the same correspondence in another physical property, viz., the densities of their aqueous solutions containing the same proportion of acid. The densities of 2 per cent. solutions of hydrochloric and hydriodic acids appear to be respectively 1·0104 and 1·0143, at 60° F., and that of hydrobromic acid will obviously be an intermediate number. The same acids are also known to differ considerably in the boiling points of solutions containing the same proportion of acid. A considerable diversity of physical properties appears here to be compatible with equal diffusibility in substances which are isomorphous.

1439. Bromine, it will be seen from the table, diffuses less rapidly than hydrobromic acid. And hydrocyanic acid appears less diffusive than hydrochloric acid; the former acid does not, therefore, belong to the same class of diffusive substances as the latter.

1440. The usual approach to equality of diffusion between the chlorids and nitrates is observable in hydrochloric and nitric acids, at least in the 1 and 2 per cent. solutions; the wide divergence between these two acids, in the 8 per cent. solution, is produced by the remarkably increased diffusion of hydrochloric acid in that high proportion.

1441. The diffusibility of different strengths of sulphuric acid appears to be pretty uniform, but with a slight tendency to increase in higher proportions, like hydrochloric acid; but it is greatly inferior in velocity of diffusion to this latter acid.

1442. The diffusibility of acetic acid diminishes with its concentration; it is evidently considerably less diffusive than sulphuric acid.

1443. The alkaline hydrates have a higher diffusibility than their salts; they are twice as diffusive as the sulphates of the same bases, and four times as diffusive as the sulphates of magnesia and lime. The salts of potash and ammonia, of the same acid, have an equal diffusibility, which is greater than the diffusibility of the corresponding salts of soda.

1444. At the same temperature, the diffusion of nitrate of strontia almost coincides with that of the isomorphous nitrate of baryta. And the results throughout for nitrate of lime are almost identical with those of nitrate of baryta, although these two salts differ greatly in solubility, and the one is a hydrated and the other an anhydrous salt.

Of the two isomorphous salts, acetates of lead and baryta, that of the greatest atomic weight sensibly exceeds the other in diffusibility.

1445. Alcohol does not appear to belong to the same class of diffusive substances as acetic acid, which might be expected from their similarity of composition, but possesses a considerably lower diffusibility.

1446. Corresponding salts of two of the vegeto-alkalies are found to be equidiffusive. The diffusion of the salts of these organic bases in 11·43 days is exceeded by the diffusion of chloride of ammonium or potassium in 5·71 days, or half the former time. The vegeto-alkalies appear thus to be divided from ammonia and potash.

1447. *Diffusion of mixed salts.*—When two salts can be mixed together without combining, it is to be expected that they will be diffused separately, and independently of each other, each salt following its special rate of diffusion.

(1.) Anhydrous sulphate of magnesia and sulphate of water (oil of vitriol), 1 part of each, were dissolved together in 10 parts of water, and the solution allowed to diffuse for four days and eight days at 61°·5.

The water jar was found to have acquired,—

	4 days.	8 days.
Sulphate of magnesia -	5·60 grs.	9·46 grs.
Sulphate of water -	21·92 ,,	29·32 ,,
	27·52 ,,	38·78 ,,

It is obvious that the inequality should be greatest in the first period of diffusion, or with the initial diffusion, as it actually appears above, and become less and less sensible as the proportion of the low diffusive salt comes to be increased in the solution phial. In former experiments upon the solution of sulphate of magnesia *alone* in water, as 1 salt to 10 water, compared with sulphate of water, also as 1 to 10, the disparity in the diffusion of these two salts was less considerable, being only as 1 to 2·385, instead of 1 to 3 or 4.

(2.) A solution was also diffused of 1 part of anhydrous sulphate of soda and 1 part of chloride of sodium, in 10 parts of water, for four days, at 61°·5. The salt which diffused out in that time consisted of—

Sulphate of soda - - - -	9·48 grs.
Chloride of sodium - - - -	17·80 ,,
	27·28 ,,

The sulphate of soda in the last experiment had begun to crystallize in the solution phial, from a slight fall of temperature, before the diffusion was interrupted; a circumstance which may have contributed to increase the inequality of the proportions diffused of these two salts.

(3.) A solution of equal weights of anhydrous carbonate of soda and chloride of sodium, namely, of 4 parts of the one salt and 4 parts of the other, to 100 water, was diffused from 3 four-ounce phials of 1·25 inch aperture, at a mean temperature of 57°·9, and for seven days. The diffusion product amounted to 17·10, 17·58, and 18·13 grs. of mixed salt in the three experiments. The analysis of the last product of 18·13 grs. gave,—

Carbonate of soda	- -	5·68 grs.	31·33
Chloride of sodium	- -	12·45 „	68·67
		18·13 „	100·00

Here the carbonate of soda presents a diffusion less than one-half of that of chloride of sodium. The difference is again greater than the peculiar diffusibilities of the same salts as they appear when the salts are separately diffused. For in experiments made in the same phials with solutions of 4 parts of each salt singly to 100 water, but with a lower temperature by 3°·6, namely, at 54°·3, the diffusion product of the carbonate of soda was 7·17 and 7·34 grs. in two experiments, of which the mean is 7·25 grs.; while the diffusion product of the chloride of sodium was 11·18 and 10·73 grs. in two experiments, of which the mean is 10·95 grs. The quantity of chloride of sodium diffused being taken at 100 in both sets of experiments, we have diffused,—

Of carbonate of soda, 66·18 when diffused singly;
„ „ 45·64 when diffused with chloride of sodium.

The least soluble of the two salts appears in all cases to have its diffusibility lessened in the mixed state. The tendency to crystallization of the least soluble salt must evidently be increased by the admixture. Now it is this tendency, or perhaps more generally the increased attraction of the particles of a salt for each other, when approximated by concentration, which most resists the diffusion of a salt, and appears to weaken the diffusive force in mixtures, as it is also found to do so in a strong solution of a single salt.

(4.) Equal weights of nitrates of potash and ammonia, dissolved in five times the weight of the mixed salts of water, and diffused for eight days, gave in two experiments,—

		At 59°·4.	At 52°·6.
Nitrate of potash	-	28·39 grs.	25·88 grs.
Nitrate of ammonia	-	36·16 „	30·36 „
		64·55 „	56·24 „

The inequality in the diffusion of these two nitrates is singular, considering that in solutions of 1 salt to 10 water, they appeared before to be equally diffusive. But when the salts are mixed, and present in the water in the proportion of 1 salt to 5 water, they no longer diffuse in equal proportions; in this case the solution of nitrate of potash was nearly a saturated one, while that of nitrate of ammonia was far from being so; the first has its diffusibility, in consequence, impaired, and falls considerably below the second.

The relatively diminished diffusibility of sulphate of magnesia, when associated with sulphate of water, is probably connected with a similar circumstance; sulphate of magnesia being less soluble in dilute sulphuric acid than in pure water.

(5). The salt which diffused from a strong solution of sulphates of zinc and magnesia, consisting of 1 part of each of these salts in the anhydrous state, and 6 parts of water, did not consist of the two salts in exactly equal proportions. The mixture of salts diffused for eight days gave the following results:—

	Exp. I.	II.	III.
Sulphate of zinc -	8·12 grs.	7·49 grs.	8·12 grs.
Sulphate of magnesia	8·68 „	8·60 „	8·75 „
	16·80 „	16·09 „	16·87 „

There is therefore always a slight but decided preponderance of sulphate of magnesia, the more soluble salt, in the diffusion product. These last experiments were made at an early period of Mr. Graham's researches, with another object in view, namely, to ascertain whether, in closely related salts, such as the sulphates of magnesia and zinc, the two salts might be elastic to each other, like particles of one and the same salt, so that one salt might possibly suppress the diffusion of the other, and diffuse alone for both. The experiments lend no support to such an idea.

It appears from all the preceding experiments, that the inequality of diffusion which existed is not diminished, but exaggerated in mixtures; a curious circumstance, which has also been observed of mixed gases.

1448. *Separation of salts of different bases by diffusion.* —It was evident from the preceding experimental facts that inequality of diffusion supplies a method for the separation, to a certain extent, of some salts from each other, analogous in principle to the separation of unequally volatile substances by the process of distillation. The potash salts appearing to be always more diffusive than the corresponding soda salts. It follows, that if a mixed solution of two such salts be placed in the solution phial, the potash salt should escape into the water atmosphere in largest proportion, and the soda salt be relatively concentrated in the phial. This anticipation was fully verified.

(1.) A solution was prepared of equal parts of the anhydrous carbonates of potash and soda in five times the weight of the mixture of water. Diffused from a small thousand-grain phial of 1·1 inch aperture, into 6 ounces of water, for nineteen days, at about 60° F., the mixed salt amounted at this time to 8·58 grs.; the analysis of the mixture gave,—

Carbonate of soda - - -	3·12 grs.	36·37
Carbonate of potash - -	5·46 „	63·63
	8·58 „	100·00

(2.) A partial separation of the salts of sea water was effected in a similar manner.

Chemical analysis, which gives with accuracy the proportions of acids and bases in a solution, furnishes no means of deciding how these acids and bases are combined, or what salts exist in solution. But it is possible that light may be thrown on the constitution of mixed salts, at least when they are of unequal diffusibility, by means of a diffusion experiment. With reference to sea water, for instance, it has been a question in what form the magnesia exists, whether as chloride or as sulphate, or how much exists in the one form, and how much in the other. Knowing, however, the different rates of diffusibility of these two salts, which is nearly chloride 2, and sulphate 1, and their relation to the diffusibility of chloride of sodium, we should be able to judge from the proportion in which the magnesia travels in company with chloride of sodium, whether it is travelling in the large proportion of chloride of magnesium, in the small proportion of sulphate of magnesia, or in the intermediate proportion of a certain mixture of chloride and sulphate. But here we are met by a difficulty. Do the chloride of magnesium and sulphate of magnesia necessarily pre-exist in sea water in the proportions in which they are found to diffuse? May not the more easy diffusion of chlorides determine their formation in the diffusive act, just as evaporation determines the formation of a volatile salt—producing carbonate of ammonia, for instance, from chloride of ammonia and carbonate of lime? We shall see immediately that liquid diffusion, as well as gaseous evaporation, can produce chemical decompositions.

1449. *Decomposition of salts by diffusion.*—(1.) From a solution of bisulphate of potash, saturated at 68°, and of density 1·28, from a six-ounce phial of 1·175 inch aperture, into 20 ounces of water, the period of diffusion extending to fifty days, there diffused out,—

Sulphate of potash -	20·37	Bisulphate of potash.
Sulphate of water -	11·47	
Sulphate of water -	12·77	
	44·61	

It thus appears that the bisulphate of potash undergoes decomposition in diffusing, and that the acid diffuses away to about double the extent, in equivalents, of the sulphate of potash.

(2.) A similar experiment was made with another double sulphate of greater stability, common potash alum. A 4 per cent. solution of anhydrous alum at 64° was diffused from a six-ounce phial into 24 ounces of water for eight days. The quantity of salt diffused in that time amounted only to 7·48 grs. It contained 1·06 grs. alumina, which is equivalent to 5·33 grs. of alum. The diffused salt gave off no acid vapours at 600°; we may therefore suppose the excess of salt which is diffused to be sulphate of potash; the diffusion product will therefore be—

Alum - - - -	5·33 grs.	71·26
Sulphate of potash -	2·15 „	28·74
	7·48 „	100·00

1450. The following question presented itself to Mr. Graham for solution,—Is it possible to decompose the sulphates of potash and soda, and the chlorides of potassium and sodium, by means of lime, when the affinity of that base for an acid is aided by the high diffusibility of the hydrate of potash or of soda?

(1.) A solution was made of 1 part of sulphate of potash in 100 parts of lime water, with which the phials were filled, and placed to diffuse in jars containing lime water, instead of water simply, for the usual period of seven days. There diffused out,—

	From 4 phials.	
Hydrate of potash - -	2·19 grs. -	21·66
Sulphate of potash - -	7·94 „ -	78·34
	10·13 „	100·00

From this it will be seen that more than a fifth part of the diffused salt is hydrate of potash, and consequently the sulphate of potash has suffered decomposition to that extent.

(2.) Sulphate of soda, dissolved in lime water, was diffused into lime water in a precisely similar series of experiments. The diffusion product obtained in a set of four cells consisted of,—

Hydrate of soda - -	0·90 grs. -	11·45
Sulphate of soda - -	6·87 „ -	88·55
	7·77 „	100·00

It will be seen from this experiment that the amount of hydrate of soda formed and diffused amounts, on an average, to about 12 per cent. of the whole diffused; yet this is only about half-weight of the hydrate of potash which was formed and diffused. Now it might justly be expected that it would require a less powerful affinity to decompose sulphate of soda than sulphate of potash; the result must therefore be referred to the superior diffusibility of the hydrate of potash.

(3.) Similar solutions of 1 per cent. of chlorides of potassium and sodium in lime water were diffused into lime water.

Eight cells of chloride of potassium gave 25·51 grains of diffused salt, containing only 0·04 grain of hydrate of potash.

Eight cells of chloride of sodium gave 20·77 grains of diffused salt, containing no more than 0·08 grain of hydrate of soda.

It is thus seen that the decomposition of the alkaline chlorides is so small as to be barely sensible, not exceeding, in the most favourable case, more than $\frac{1}{300}$th part of the salt diffused. Lime, therefore, appears incapable although aided by diffusion, to decompose the chlorides of potassium and sodium to a sensible extent.

(4.) Carbonate of lime, dissolved in carbonic acid water, or a saturated solution of bicarbonate of lime, was applied to form a 1 per cent. solution of sulphates of potash and soda. These solutions were diffused from the phials into pure water, as the liquid atmosphere of the jars. Decomposition of the alkaline sulphate always took place, but to a less extent than when hydrate of lime was employed. The proportion of potash salts diffused in two pairs of cells was 4·86 and 5·84 grains, of which 0·26 and 0·30 grains was carbonate of potash, or 5·35 and 6·2 per cent. of carbonate of potash.

The proportion of soda salts diffused in two pairs of cells was 3·40 and 3·87 grains, of which 0·26 and 0·29 grains was carbonate of soda, or 7·65 and 7·67 per cent. of carbonate of soda. The excess of carbonate soda diffused over the carbonate of potash in these experiments, Graham remarks, is probably accidental.

1451. The experiments on the decomposition of an alkaline sulphate by means of carbonate of lime, aided by diffusion, are chiefly interesting as they illustrate a decomposition which may occur among the salts of the soil, and with the formation of an alkaline carbonate, form a reaction between carbonate of lime and an alkaline sulphate; although the solutions may be too dilute to admit of any separation of sulphate of lime in the solid state.

1452. But the decomposition of the chlorides of potassium and sodium is a more important problem, Graham observes, than that of the sulphates of potash and soda. We have seen that the direct diffusion of these chlorides with hydrate of lime only yielded a trace of fixed alkali; and when concentrated solutions of the chlorides were employed not a trace of alkali was formed. Bicarbonate of lime had no greater effect upon these chlorides. But the conjoint action of lime water and the sulphate of lime upon these chlorides gave better results; but even in this case, when cold solutions were employed, only the faintest trace of alkali was detected. To enable the hydrate and sulphate of lime to act upon the chloride of sodium, it was found necessary to heat the solution before diffusion.

1453. The solution of sulphate of lime, with an addition of 2 per cent. of chloride of sodium, was kept at the boiling point for half an hour. No deposition of sulphate of lime occurred then, or after the liquid cooled. Two or three days afterwards, the solution was mixed with an equal volume of lime-water, and two phials of the solution were diffused into pure water for 7 days and 18 hours. The lime found in the water was equal to 1·01 grs. of carbonate of lime. The alkaline compounds amounted to 6·14 grs., and contained 0·646 grs. of hydrate of soda, and 0·373 grs. of sulphate of soda. It is difficult to decide in what form the lime reached the water jar, but this earth was probably diffused out of the solution phial, partly as hydrate of lime, partly as sulphate of lime, but principally as chloride of calcium. Graham observes, that with a smaller quantity of chloride of sodium than 2 per cent. in the original mixture, the alkali, although not increased in absolute quantity, might no doubt come to form a considerably larger proportion of the diffusion product.

1454. The experiments throw a curious light upon the condition of mixed salts. It follows, from the absence of hydrate of soda in the diffusion product of the first experiments, that cold solutions of sulphate of lime and chloride of sodium may be mixed without decomposition, or without any sensible formation of sulphate of soda. But on heating, this change is induced, and it is permanent; sulphate of soda is formed, and continues to exist in the cold solution; for it is the decomposition of that salt alone, hydrate of lime, which appears to afford the diffused hydrate of soda. More than one condition of equilibrium is therefore possible for mixed solutions of sulphate of lime and chloride of sodium. It would be interesting to submit such a mixture to a diffusion experiment, after being kept for different periods. The effects of time and temperature are so often convertible, that we might anticipate a gradual formation of sulphate of soda. If such be the case, we have an agency in the soil, by which the alkaline carbonates required by plants may be formed from the chlorides of potassium and sodium, as well as from the sulphates of potash and soda; for the sulphate of lime, generally present, will convert those chlorides into sulphates.

1455. The mode in which the soil of the earth is moistened by rain is peculiarly favourable to separations by diffusion. The soluble salts of the soil may be supposed to be carried down together, to a certain depth, by the first portion of rain which falls, while they find afterwards an atmosphere of nearly pure water, in the moisture which falls last and occupies the surface stratum of the soil. Diffusion of the salts upwards into this water, with its separations and decompositions, must necessarily ensue. The salts of potash and ammonia, which are most required for vegetation, possess the highest diffusibility, and will rise first. The pre-eminent diffusibility of the alkaline hydrates may also be called into action in the soil by hydrate of lime, particularly as quick-lime is applied for a top-dressing to grass lands.

1456. *Diffusion of double salts.*—How is the diffusion of two salts affected by their condition of combination as a double salt? A solution of the double sulphate of magnesia and potash, in the proportion of 100 water to 4 of the anhydrous salt, was diffused in the four-ounce diffusion phials, of 1·25 inch aperture, for seven days at 57°·9 F.; the diffusion product of the double salt amounted to 7·95 grs.

1457. The constituent salts, sulphate of magnesia and sulphate of potash, were now dissolved separately, in the proportions in which they existed in the double salt; the separate diffusion of the sulphate of magnesia was 2·20 grs., and the separate diffusion of the sulphate of potash was 5·78 grs., the circumstances of the experiments being the same as those of the double salt. The result is, that the separate diffusion of the constituent salts is almost identical with their diffusion when combined as a double salt:—

Diffusion of the double sulphate of magnesia and potash - - - - - -	7·95 grs.

Diffusion of equivalents of sulphate of magnesia and sulphate of potash in separate cells	7·98 grs.

It would thus appear that the diffusibility of this double salt is the sum of the separate diffusions of its constituent salts.

1458. It has been a question whether a double salt is formed at once when its constituent salts are dissolved together, or not till the act of crystallization of the compound salt. Equivalents of the same two sulphates, making up 4 parts, were dissolved together, without heat, in 100 water. Now the diffusion from this mixture, which has the composition of the preceding solution of the double salt, exhibited notwithstanding a sensibly different result of diffusion; the diffusion of the mixture being 7·30 grs., whilst the diffusion of the double salt was 7·95 grs. Hence a strong presumption that the mixed salts last diffused were not combined, and that the double sulphate of magnesia and potash is not necessarily formed immediately upon dissolving together its constituent salts.

1459. In experiments of a similar nature made upon the double salt, sulphate of copper and potash, and upon a mixture of the two sulphates newly dissolved together, a similar result was obtained. While the diffusion of the mixed salts was 25·6 grs., that of the same weight of the combined salts (the double sulphate) was 30 grs. The double salt appears more diffusible, in both cases, than its mixed constituents.

1460. These double salts appear to dissolve in water without decomposition, although the single salts may meet in solution without combining. Hence, in a mixture of salts we may have more than one state of equilibrium possible. And when a salt like alum happens to be dissolved in such a way as to decompose it, the constituents are not necessarily re-united by subsequent mixing. Many practices in the chemical arts, which seem empirical, have their foundation, possibly, in facts of this kind.

1461. *Diffusion of one salt into the solution of another salt.*—It was curious and peculiarly important, in reference to the relation of liquid to gaseous diffusion, to find whether one salt, A, would diffuse into water already charged with an equal or greater quantity of another salt, B, as a gas, *a*, freely diffuses into the space already occupied by another gas, *b*; the gas, *b*, in return diffusing at the same time into the space occupied by *a*; or whether, on the contrary, the diffusion of the salt, A, is resisted by B. The latter result would indicate a neutralization of the water's attraction for a second salt, which would divide entirely the phenomena of liquid from those of gaseous diffusion.

(1.) A solution of 4 parts of carbonate of soda to 100 water, of density 1·0406, was found to diffuse with equal rapidity into a solution of 4 parts of chloride of sodium to 100 water, having the density 1·0282, as into pure water.

(2.) The same solution of carbonate of soda was diffused into a solution of sulphate of soda (a salt more similar to the carbonate in solubility and composition), containing 4 per cent., and of density 1·0352, there was a small reduction in the quantity of carbonate of soda diffused, amounting to one-eighth of the whole. The sulphate of soda, therefore, exercised a positive interference in checking the diffusion of the carbonate to that extent. So small and disproportionate an effect, however, is scarcely sufficient to establish the existence of a mutual elasticity and resistance between these two salts.

(3.) Still it might be said, May not the diffusion of one salt be resisted by another salt which is strictly isomorphous with the first? The diffusion of a 4 per cent. solution of nitrate of potash, however, was found not to be sensibly reduced by the presence of 4 per cent. of nitrate of ammonia in the water atmosphere, although these two salts are closely isomorphous. They are still, therefore, inelastic to each other, like two different gases.

1462. These experiments were made upon dilute solutions, and it is not at all improbable that the result may be greatly modified in concentrated solutions of the same salts, or when the solutions approach to saturation. But there is reason to apprehend that the phenomena of liquid diffusion are exhibited in the simplest form by dilute solutions, and that concentration of the dissolved salt, like compression of a gas, is often attended with a departure from the normal character.

1463. On approaching the degree of pressure which occasions the liquefaction of a gas, an attraction appears to be brought into play which impairs the elasticity of the gas; so, on approaching the point of saturation of a salt, an attraction of the salt-molecules for each other, tending to produce crystallization, comes into action, which will interfere with and diminish that elasticity or dispersive tendency of the dissolved salt which occasions its diffusion.

1464. We are perhaps justified in extending the analogy a step farther, between the characters of a gas near its point of liquefaction and the conditions which may be assigned to solutions. The theoretical density of a liquefiable gas may be completely disguised under great pressure. Thus, under a reduction by pressure of 20 volumes into 1, while the elasticity of air is 19·72 atmospheres, that of carbonic acid is only 16·70 atmospheres, and the deviation from their normal densities is in the inverse proportion. Of salts in solution, the densities may be affected by similar causes, so that although different salts in solution really admit of certain normal relations in density, these relations may be concealed, and not directly observable.

1465. The analogy of liquid diffusion to gaseous diffusion and vaporization, is borne out in every character of the former which has been examined. Mixed salts appear to diffuse independently of each other, like mixed gases, and into a water atmosphere, already charged with another salt, as into pure water. Salts also are unequally diffusible, like the gases, and separations, both mechanical and chemical (decompositions), are produced by liquid as well as by gaseous diffusion. But it still remains to be found whether the diffusibilities of different salts are in any fixed proportion to each other, as simple numerical relations are known to prevail in the diffusion velocities of the gases from which their densities are deducible.

1466. *Diffusion of salts of potash and ammonia.*

Solutions were prepared of the various salts in a pure state, in certain fixed proportions,—namely, 2, 4, 6⅔,—and 10 parts of salt to 100 parts of water by weight. The density of the solutions was determined at 60°. The diffusion products are expressed in grains.

Substance.	Temp. F.	2.	4.	6⅔.	10.
Carbonate of potash -	64°·2	5·45	10·25	16·67	24·69
Sulphate of potash -	,,	5·52	10·57	17·17	23·62
Sulphate of ammonia	,,	5·58	10·51	16·79	22·20
Chromate of potash -	64°·1	5·77	11·19	17·60	24·75
Acetate of potash -	,,	5·85	10·70	16·48	24·85
Bicarbonate of potash	,,	5·81	11·01	—	—
Bichromate of potash	64°·5	5·65	11·49	—	—

It is singular to find that salts differing so much in constitution and atomic weight as the chromate and bichromate of potash, may be confounded in diffusibility. The bicarbonate of potash also exhibits a considerable analogy to the carbonate, but resembles still more closely the acetate. It is thus obvious that similarity or equality of diffusion is not confined to the isomorphous groups of salts.

Substance.	Temp. F.	2.	4.	6⅔	10.
Nitrate of potash -	65°·9	7·47	13·97	22·37	32·49
Nitrate of ammonia -	,,	7·73	14·48	22·74	34·22
Chloride of potassium	66°·2	7·70	15·29	24·87	36·39
Chloride of ammonium	,,	7·81	14·60	24·30	36·53

1467. The salts of potash thus appear to fall into two groups, the members of which have a nearly equal diffusibility, at least from weak solutions, such as 1 or 2 per cent. Of what may be called the sulphate of potash class the diffusion from 1 per cent. solutions was as follows:—

Diffusion of 1 *per cent. solutions at* 58°·5.

Carbonate of potash - - -	2·63 grs.
Sulphate ,, - - -	2·69 ,,
Acetate ,, - - -	2·68 ,,
Chromate ,, - - -	2·83 ,,
Bicarbonate ,, - - -	2·81 ,,
Bichromate ,, - - -	2·88 ,,

Mr. Graham remarks, that the divergence from each other of two salts so closely isomorphous as sulphate and chromate of potash, in the proportion of 100 to 105·2, is certainly remarkable, unless due to a slight decomposition of the latter.

Diffusion of 1 *per cent. solutions of salts of the nitre class at* 64°·5.

Nitrate of potash	3·72 grs.
Nitrate of ammonia	3·75 „
Chloride of potassium	3·88 „
Chloride of ammonium	3·89 „
Chlorate of potash	3·66 „

1468. What is the relation between these two groups of salts?

The diffusion of 4 per cent. solutions of carbonate and nitrate of potash was repeated at a temperature rising gradually from 63° to 65° during the seven days of the experiment, with a mean of 64°·1. The diffusion products of the carbonate, were 10·31, 10·05, and 10·44, in three cells; mean, 10·27 grs. Of the nitrate, 13·98, 13·86, and and 13·60 grs.; mean, 13·81 grs. There is thus a diffusion, in equal times, of—

Carbonate of potash	10·27	1
Nitrate of potash	13·81	1·3447

But the numbers so obtained cannot be fairly compared, owing to the diminishing progression in which the diffusion of a salt takes place. Thus, when the diffusion of nitrate of potash was interrupted every two days, as in the experiment with chloride of sodium, the progress of the diffusion for eight days was found to be as follows in a 4 per cent. solution, with a mean temperature of 66°:—

Nitrate of potash diffused in	first two days,	4·54 grs.
„ „	second „ „	4·13 „
„ „	third „ „	4·06 „
„ „	fourth „ „	3·18 „
		15·91

The absence of uniformity in this progression is, no doubt, chiefly due to the want of geometrical regularity in the form of the neck and shoulder of the solution-phial. A plain cylinder, as the solution cell, might give a more uniform progression, but would increase greatly the difficulties of manipulation.

The diffusion of carbonate of potash will, no doubt, follow a diminishing progression also; but there is this difference, that the latter salt will not advance so far in its progression, owing to its smaller diffusibility, in the seven days of the experiment, as the more diffusible nitrate does. The diffusion of the carbonate will thus be given in excess, and as it is the smaller diffusion, the difference of the diffusion of the two salts will not be fully brought out.

The only way in which the comparison of the two salts can be made with perfect fairness, is to allow the diffusion of the slower salt to proceed for a longer time,--till, in fact, the quantity diffused is the same for this as for the other salt, and the same point in the progression has, therefore, been attained in both; and to note the time required. The problem takes the form of determining the *times of equal diffusion* of the two salts. This procedure is the more necessary from the inapplicability of calculation to the diffusion progression.

Further, allowing the *times of equal diffusion* to be found, it is not to be expected that they will present a simple numerical relation.

Recurring to the analogy of gaseous diffusion, the times in which equal volumes or equal weights of two gases diffuse are as the square roots of the densities of the gases. The times, for instance, in which equal quantities of oxygen and hydrogen escape out of a vessel into the air, in similar circumstances, are as 4 to 1; the densities of these two gases as 16 to 1; or the times of equal diffusion of oxygen and protocarburetted hydrogen are as 1·4142 to 1, that is, as the square root of 2 to the square root of 1; the densities of these gases being 16 and 8, which are as 2 to 1. The densities are the squares of the equal diffusion times. It is not, therefore, the times themselves of equal diffusion of two salts, but the squares of those times, which are likely to exhibit a simple numerical relation.

While the 4 per cent. solution of nitrate of potash was diffused, as usual, for 7 days, the corresponding solution of carbonate of potash was now allowed to diffuse for 9·90 days,—times which are as 1 to 1·4142, or as 1 to the square root of 2.

The results were as follows. Diffused of—

Nitrate of potash, at 64°·1. in 7 days -	13·81 grs.	100
Carbonate of potash, at 64°·3, in 9·9 days - - - - - - -	13·92 „	100·8
Difference - -	0·11	

Seven and 9·90 may therefore be considered as the times of equal diffusion indicated for nitrate and carbonate of potash.

The explanation of such a relation suggested by gaseous diffusion is that the molecules of the two salts, as they exist in solution, have different densities; that of nitrate of potash being 1, and that of carbonate of potash 2. We are thus led to ascribe densities to the *solution molecules* of the salts, conceived on the analogy of vapour densities. The two salts in question are related exactly like protocarburetted hydrogen gas, of density 1, to oxygen gas, of density 2. The parallel would be completed by supposing that the single volume of oxygen to be diffused was previously mixed with 100 volumes of air (or any other diluting gas), while the two volumes of protocarburetted hydrogen were also diluted with 100 volumes of air,—the diluting air here representing the water in which the salts to be diffused are dissolved in the solution phial. The time in which a certain quantity of protocarburetted hydrogen would come out from a vessel containing 1 per cent. of that gas being 1 (the square root of density 1), the time in which an equal quantity of oxygen would diffuse out from a similar vessel containing 1 per cent. also, would be 1·4142 (the square root of density 2).

The existence of the relation between the sulphate and nitre class of potash salts was also tested by employing sulphate of potash and chromate of potash in place of the carbonate. Preserving the ratio in the times of diffusion for the two classes of salts, the actual times were varied in duration, in three series of experiments, as 1, 2, and 3: 1 per cent. solutions were employed in each of the experiments:—

3·5 and 4·95 days.	Nitrate of potash, at	47°·2	3·50 grs.	100
	Sulphate „ „	47°·3	3·50 „	100
7 and 9·9 days.	Nitrate of potash, at	48°·6	6·04 „	100
	Sulphate „ „	49°·1	6·20 „	102·65
	Chromate „ „	49°·1	6·29 „	104·14

10·5 and 14·85 days.	Nitrate of potash, at 48°	8·74 grs.	100
	Sulphate „ „ 48°·6	8·79 „	100·57

The concurring evidence of these and other series of experiments which Mr. Graham made, is strongly in favour of the assumed relation of 1 to 1·4142, between the times of equal diffusion for the nitrate and sulphate of potash: and, consequently, of the times for the two classes of potash salts, of which the salts named appear to be types. The same experiments are also valuable as proving the similarity of the progression of diffusion in two salts of unequal diffusibility.

A 1 per cent. solution of pure fused hydrate of potash was diffused for 4·95 days at a mean temperature of 53°·7; the diffused product was 3·06 grains for a single cell.

A 1 per cent. solution of nitrate of potash was diffused for 7 days at a mean temperature of 53°·6; the diffused product was 3·11 grains for a single cell.

The diffusion of nitrate of potash being 100, that of the hydrate of potash is 98·2,—numbers which are sufficiently in accordance; but the times were as 1 to 1·4142, and their squares as 1 to 2. We thus appear to have for the salts of potash a close approximation to the following simple series of times of equal diffusion with the squares of these times:—

	Times.	Squares of times.
Hydrate of potash - -	1 - -	1
Nitrate of potash - -	1·4142 - -	2
Sulphate of potash - -	2 - -	4

The only salts of soda which have yet been diffused in a sufficient variety of circumstances, are the carbonate and sulphate. These salts appear to be equidiffusive, but to diverge, notwithstanding, more widely in solutions of the higher proportions of salt than the corresponding potash salts. It is a question whether this increased divergence is not due to the less solubility of the soda salts, and the nearer approach, consequently, to their points of saturation in the stronger solutions.

The mean results at 64° were as follows:—

	2.	4.	6¼.	10.
Carbonate of soda -	4·14	7·78	12·22	16·88
Sulphate of soda -	4·31	8·17	13·50	19·14

Diffusion of 1 *per cent. solutions at* 64°·9.

Carbonate of soda	2·32 grs.	100
Sulphate of soda	2·38 „	102·58

The diffusion of the carbonate of soda was further compared with the nitrate of the same base, to find whether their times of equal diffusion are related, like those of the corresponding potash salts.

1 per cent. solution of nitrate of soda, in 7 days, at 66°·9, in 4 cells	11·73 grs.	100
1 per cent. solution of carbonate of soda, in 9·9 days, at 66°·9	11·62 „	99·06
2 per cent. solution of nitrate of soda, in 7 days, at 54°·3	10·10 „	100
2 per cent. solution of carbonate of soda, in 9·9 days	9·95 „	98·51

It appears, therefore, that the times of equal diffusion of the nitrate and carbonate of soda are related, like those of the nitrate and carbonate of potash, or as the square root of 1 and 2, that is, as 1 to 1·4142.

It appeared probable, from the experiments which Mr. Graham had already made, that if any relation, in the times of equal diffusibility, existed between the corresponding salts of potash and soda, it was that of the square root of 2 to the square root of 3. They were accordingly diffused for times having this ratio, namely, the nitrate of potash for 7 days, the nitrate of soda for 8·57325 days; the sulphate and carbonate of potash for 9·9 days, and the sulphate and carbonate of soda for 12·125 days. The experiments proved that these times were rightly chosen, for the diffusion of the two nitrates and two sulphates coincided; the two carbonates fell about 3·4 per cent. below the sulphates and nitrates, but they agreed perfectly with each other, showing a uniformity in their irregularity. This deviation of the carbonates would appear to be essential, as it was observed on every occasion they were compared with the sulphates.

1469. *Crystalloid and colloid substances.*—We have already learned that different substances diffuse in an aqueous atmosphere *unequally* in equal times. The diffusive power of some substances, albumen for instance, is very low compared with the diffusive power of other substances, such as chloride of sodium and hydrochloric acid. Mr. Graham has pointed out that just as bodies can be divided into two classes, the volatile and non-volatile, according as they are or are not endowed with the property of volatility, so in like manner substances can be divided into two classes according to the degree of diffusive power they possess in the liquid state; and this difference in diffusive power appears to correspond with differences in molecular constitution of a fundamental nature.

1470. The substances which have a comparatively high diffusive power have generally the power of crystallizing. When in a state of solution, they are held by the solvent with a certain force. The solution is generally free from viscosity, and always sapid. Their reactions are energetic, and quickly effected. They differ in the degree of diffusiveness. Thus hydrate of potash may be said to possess double the velocity of diffusion of sulphate of potash; and sulphate of potash, again, double the velocity of sugar, alcohol, and sulphate of magnesia. Mr. Graham has proposed to designate the substances forming this class *crystalloids*.*

1471. Substances of very low diffusive power belong to a different order of chemical substances. The substances comprising this class have little if any tendency to crystallize, and they affect a vitreous structure. They are distinguished by the gelatinous character of their solid hydrates. In these hydrates the water is held by such a feeble force that the crystalloids can decompose them by removing it. The crystalloids, as we shall learn presently, by this appropriation obtain a medium for diffusing in and through these solid compounds.

Although these substances of low diffusive power are often largely soluble in water, they are held in solution by a feeble power. They are generally precipitated from their solution by the addition of any crystalloid. The solution of these bodies has always a certain degree of viscosity, or gumminess, when concentrated. They appear to be insipid, or wholly tasteless, unless when they undergo decomposition on the palate, and rise to sapid crystalloids. Gelatine has been taken as the type of this class, and they have been designated *colloids*, from *collin*, the best sort of gelatine. Among the colloids rank hydrated silicic acid and a number of soluble hydrated metallic peroxides, of which little has hitherto been known; also starch, the vegetable gums, and dextrin, caramel, tannin, albumen, and animal and vegetable extractive matters.

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* The bodies belonging to this class are not all crystalline, for hydrochloric acid and alcohol belong to this class.

1472. As we can separate, by means of distillation or evaporation, a volatile from a less volatile body, so by the aid of diffusion we can separate one substance more or less completely from another. Mr. Graham has latterly employed, in place of the process we have already described, and which he terms "vial-diffusion," a still more simple arrangement, in which he dispenses with the inner vessel, and employs only a plain cylindrical glass jar, 6 inches deep and 3·45 inches wide. This is graduated, from the bottom up to within an inch of the top, into sixteen equal parts. Distilled water is first introduced into the jar, so as to occupy fourteen of the divisions, and then, by means of a pipette with a small aperture, the liquid to be diffused is slowly and carefully conveyed to the bottom of the vessel, so as to form a distinct stratum, occupying two divisions; no sensible intermixture of the two liquids takes place during the delivery, if sufficient time (five or six minutes) is occupied in allowing the liquid to flow out of the pipette. The spontaneous diffusion, which immediately commences, is allowed to go on for a period of several days in an apartment of a constant, or nearly constant, temperature. Each stratum, or division, is then separately examined; this is effected by drawing off very carefully, commencing at the top, a division at a time, by means of a small syphon. A species of cohobation has been the consequence of unequal diffusion, the most rapidly diffusive substance being isolated more and more as it ascended. The higher the water column, sufficient time being always given to enable the most diffusive substance to appear at the summit, the more completely does a portion of that substance free itself from the less diffusive substances which may be associated with it. A marked separation is effected even between substances whose difference in diffusive power is very small; as, for instance, in the separation of chloride of potassium from chloride of sodium, of which the relative diffusibilities are as 1 to 0·841. The experiments recorded in Tables VI. to XI. were obtained by this method.

TABLE VI.—*Diffusion of* 10 *per cent. solutions* (10 *grams. of substance in* 100 *cub. cent. of fluid*) *into pure water, after* 14 *days, at* 10° *C.* (50° *F.*).

Number of stratum (from above downwards).	Chloride of sodium.	Sugar.	Gum.	Tannin.
1 - -	·104	·005	·003	·003
2 - -	·129	·008	·003	·003
3 - -	·162	·012	·003	·004
4 - -	·198	·016	·004	·003
5 - -	·267	·030	·003	·005
6 - -	·340	·059	·004	·007
7 - -	·429	·102	·006	·017
8 - -	·535	·180	·031	·031
9 - -	·654	·305	·097	·069
10 - -	·766	·495	·215	·145
11 - -	·881	·740	·407	·288
12 - -	·991	1·075	·734	·556
13 - -	1·090	1·435	1·157	1·050
14 - -	1·187	1·758	1·731	1·719
15 and 16 -	2·266	3·783	5·601	6·097
	9·999	10·003	9·999	9·997

1473. The superimposed column of water being 111 millimetres (4·38 inches) in height, the chloride of sodium, it will be observed, has diffused in sensible quantity to the top, and could have risen higher, the upper layer being found to contain 0·104 gramme of salt, or 1 per cent. of the whole quantity present. The apex of the diffusion column of sugar appears to have just reached the top of the liquid in the 14 days of the experiment, for ·005 gram. only of that substance is found in the first stratum, followed by ·008, ·012, ·016, and ·030 in the following strata. The minute quantities of gum which appear shown in the 1st to the 6th stratum, which do not altogether exceed ·020 gram., are due, Mr. Graham believes, to the result of accidental dispersion; so that the gum is not carried by diffusion higher than the 7th stratum (2·2 inches). The diffusion of the tannin is even less advanced than the gum, and the quantity diffused is increased by a partial decomposition, to which tannin is liable, and which gives rise to new and more highly diffusible substances.* We learn, then, from the results of the experiments recorded in this and some of the other tables, that some substances can travel to the extreme limit of the water, whilst others can only travel a short distance in the aqueous atmosphere.

1474. Experiments continued, like those last described, for a constant time, do not exhibit the exact relative diffusibilities, although these could be obtained by proceeding to ascertain, by repeated trial, the various times required to bring about a similar distribution and equal amount of diffusion in all the salts. The numbers observed, however, may afford data for the deduction of the relative diffusibilities by calculation.

1475. A particular advantage of the new method is the means which it affords of ascertaining the absolute rate or velocity of diffusion. It becomes possible to state the distance which a salt travels per second in terms of the metre. It is easy to see that such a constant must enter into all chronic phenomena of physiology, and that it holds a place in vital science not unlike the time of the falling of heavy bodies in the physics of gravitation.

The sulphate of magnesia was anhydrous. Its diffusion is very similar to that of sugar. The fall in the rate of diffusion, on passing from the crystalloids to the colloids, gum, albumen, tannin, and caramel, is very striking. The diffusion of the caramel is the slowest of all, and does not much exceed in 14 days the diffusion of sugar in a single day. The diffused albumen did not appear to lose its coagulability, or to be otherwise altered.

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* To the low diffusibility of tannin may be ascribed the remarkably slow penetration of skins by that substance, in the ordinary operation of tanning leather.

TABLE VII.—*Diffusion of* 10 *per cent. solutions for* 14 *days.*

Number of stratum (from above downwards.)	Sulphate of magnesia, at 10°.	Albumen, at 13° to 13°·5.	Caramel, at 10° to 11°.
1 - -	·007	...	...
2 - -	·011	...	...
3 - -	·018	...	...
4 - -	·027	...	...
5 - -	·049	...	...
6 - -	·085	...	·003
7 - -	·133	...	·005
8 - -	·218	·010	·010
9 - -	·331	·015	·023
10 - -	·499	·047	·033
11 - -	·730	·113	·075
12 - -	1·022	·343	·215
13 - -	1·383	·855	·705
14 - -	1·803	1·892	1·725
15 and 16 -	3·684	6·725	7·206
	10·000	10·000	10·000

1476. It was considered useful by Mr. Graham to possess examples of the progress of diffusion, in one or two selected substances, for successive periods of time, so as to exemplify the continuous progress of diffusion in these substances. Such a chronological progress of diffusion in a particular substance, he observes, becomes a standard of comparison for single experiments on the diffusion of other substances. The substances selected were chloride of sodium and cane sugar.

TABLE VIII.—*Diffusion of a* 10 *per cent. solution of chloride of sodium in different times.*

Number of stratum.	In 4 days at 9° to 10°.	In 5 days at 11°·75	In 7 days at 9°.	In 14 days at 10°.
1	·004	·004	·013	·104
2	·004	·006	·017	·129
3	·005	·011	·028	·162
4	·011	·020	·051	·198
5	·023	·040	·081	·267
6	·040	·075	·134	·340
7	·080	·134	·211	·429
8	·145	·233	·318	·535
9	·261	·368	·460	·654
10	·436	·589	·640	·766
11	·706	·762	·850	·881
12	1·031	1·090	1·057	·991
13	1·416	1·357	1·317	1·090
14	1·815	1·697	1·527	1·187
15 and 16	4·023	3·613	3·294	2·266
	10·000	9·999	9·998	9·999

TABLE IX.—*Diffusion of a* 10 *per cent. solution of cane sugar in different times.*

Number of stratum.	In 1 day at 10°·75	In 2 days at 10°.	In 6 days at 9°.	In 7 days at 9°.	In 8 days at 9°.	In 14 days at 10°.
1	...	...	·001	·002	·002	·005
2	...	...	·002	·002	·003	·008
3	...	...	·002	·003	·003	·012
4	...	...	·002	·004	·004	·016
5	...	...	·003	·004	·007	·030
6	...	...	·005	·007	·012	·059
7	...	...	·011	·020	·031	·102
8	·002	·002	·024	·051	·072	·180
9	·002	·008	·071	·121	·154	·305
10	·005	·027	·170	·260	·304	·495
11	·024	·107	·376	·507	·555	·740
12	·133	·344	·727	·897	·858	1·075
13	·597	·930	1·282	1·410	1·365	1·435
14	1·850	1·940	1·930	1·950	1·955	1·758
15 and 16	7·386	6·641	5·392	4·760	4·674	3·783
	9·999	9·999	9·998	9·998	9·999	10·003

The scheme of the diffusion of the chloride of sodium may afford terms of comparison for the metallic salts, acids, and other highly diffusible substances, while the scheme of sugar will be found more useful in appreciating the diffusion of organic and other less diffusible substances.

1477. Comparative experiments were made with chloride of sodium and hydrochloric acid, and it was found that the diffusion of hydrochloric acid in 3 days corresponds closely with the diffusion of chloride of sodium in 7 days. Hydrochloric acid and the allied hydra acids, with other monobasic acids, are the most diffusive substances known.

The general results of several series of experiments may be expressed approximately by the following numbers:—

Approximate times of equal diffusion.

Hydrochloric acid	1
Chloride of sodium	2·33
Sugar	7
Sulphate of magnesia	7
Albumen	49
Caramel	98

Experiments were made by changing the liquid atmosphere, substituting alcohol for water; alcoholic solutions of acetate of potash, iodine, and resin, were diffused into alcohol.

1478. The following experiments on the simultaneous diffusion of two substances in the same fluid were undertaken with the object of separating salts of unequal diffusibility, and to test the application of diffusion as an analytical process. A mixture of two salts being placed at the bottom of the jar, it may be expected that the salts will diffuse pretty much as they do when they are diffused separately; the more diffusive salt travelling most rapidly, and showing itself first, and always most largely, in the upper strata. The early experiments of diffusion from phials had shown, indeed, that inequality of diffusion is increased by mixture, and the actual separation is consequently greater than that calculated from the relative diffusibilities of the mixed substances. Chlorides of potassium and sodium diffuse, according to former experiments, in the proportion of 1 to 0·841. They therefore afford the means of observing the amount of separation that may be produced by a very moderate difference in diffusibility. A mixture of 5 grams. of each salt in the usual 100 cub. cent. of water was diffused.

TABLE X.—*Diffusion of a mixture of* 5 *per cent. of chloride of potassium, and* 5 *per cent. of chloride of sodium, for* 7 *days, at* 12° *to* 13°.

Number of stratum.	Chloride of potassium.	Chloride of sodium.	Total diffusate.
1 - -	·018	·014	·032
2 - -	·025	·015	·040
3 - -	·044	·014	·058
4 - -	·075	·017	·092
5 - -	·101	·034	·135
6 - -	·141	·063	·204
7 - -	·185	·104	·289
8 - -	·252	·151	·403
9 - -	·330	·212	·542
10 - -	·349	·351	·700
11 - -	·418	·458	·876
12 - -	·511	·559	1·070
13 - -	·552	·684	1·236
14 - -	·615	·772	1·387
15 and 16 -	1·385	1·551	2·936
	5·001	4·999	10·000

1479. The table shows that the chloride of potassium is in excess in the upper strata; at the tenth the two salts are in equal proportion, and in the lower strata chloride of sodium preponderates. It is evident that the preceding experiment might be so conducted as to diffuse away the chloride of potassium, leaving below a mixture containing chloride of sodium in relative excess; or, by taking the upper strata, and submitting them to diffusion, and by continuing to repeat this diffusive rectification a sufficient number of times, a portion of the more diffusive salt might be obtained at last in a state of sensible purity.

1480. The preceding example illustrates the separation of unequally diffusive metals or bases; the following example, on the other hand, the separation of unequally diffusive acids united with a common base. It was proved in the phial experiments that chloride of sodium and sulphate of soda diffuse separately in the proportion of 1 to 0·707.

Table XI.—*Diffusion of* 5 *per cent. of chloride of sodium and* 5 *per cent. of anhydrous sulphate of soda, for* 7 *days, at* 10° *to* 10°·75.

Number of stratum.	Chloride of sodium, in grams.	Sulphate of soda, in grams.	Total diffusate, in grams.
1	·009	……	·009
2	·013	·001	·014
3	·024	·002	·026
4	·038	·003	·041
5	·060	·006	·066
6	·095	·012	·107
7	·141	·029	·170
8	·203	·059	·262
9	·278	·115	·393
10	·360	·205	·565
11	·473	·317	·790
12	·560	·507	1·067
13	·637	·694	1·331
14	·718	·909	1·627
15 and 16	1·390	2·141	3·531
	4·999	5·000	9·999

A difference in the acids, it will be seen, occasions a more sensible separation than a difference in the bases.

1481. In order to test how long the diffusion should be continued in a liquid column of limited height, the last diffusion was repeated, but the diffusion was continued for 14 days. The proportions of the two salts were not dissimilar to those obtained in the diffusion of 7 days; nothing is gained in the way of separation, therefore, by extending the diffusion period from 7 to 14 days, unless the column of fluid were increased in height at the same time.

1482. Mr. Graham remarks, "It might be worth observing whether the separation of two unequally diffusive metals can be favoured by varying the acid, or form of combination; whether, for instance, the hydrates of potash and soda would not separate to a greater extent than has been observed of the chlorides of potassium and sodium, the separate diffusibilities of the former substances being as 1 to 0·7, while that of the latter are as 1 to 0·841. I have not," he says, "pursued this branch of the subject."

1483. He goes on to remark that the separation of the same metals from each other may possibly be favoured in another manner. In the preceding, the two metals were in union with the same acid. But the metals might be used in combination with different acids, and these acids themselves might be of equal or unequal diffusibility. If of equal diffusibility, there appears no reason why the acids should influence the amount of separation. But if the acids are unlike in diffusibility, the case is not so clear. If, for instance, the potassium were in the form of chloride, and the sodium of that of sulphate, might not the diffusion of the potassium be promoted by the highly diffusive chlorine with which it is associated, and the diffusion of the soda, on the other hand, be retarded by its association with the slowly diffusive sulphuric acid? Will, in fine, the separation of the metals be greater from a mixture of chloride of potassium and sulphate of soda, or even from sulphate of potash and chloride of sodium, than from the two chlorides, or from the two sulphates? The inquiry, it will be remarked, raises the whole question of the distribution of acid and base in solutions of mixed salts. Mr. Graham instituted, as an illustration, a comparison of the diffusion of chloride of potassium mixed with sulphate of soda, with the diffusion of sulphate of potash mixed with the chloride of sodium, the salts being taken in equivalent proportions. The diffusions were strikingly similar, indeed they might be considered identical. It thus appears that the diffusion of the metals is not affected by the acid with which they are in combination. The result is quite in harmony with Berthollet's view, that the acids and bases are indifferently combined, or that a mixture of chloride of potassium and sulphate of soda is the same thing as a mixture of sulphate of potash and chloride of sodium, when the mixtures are in a state of solution. With two acids very unequal in their affinity for bases the result possibly might be very different.

1484. *Effect of temperature on diffusion.*—Diffusion is promoted by heat: separations may accordingly be effected in a shorter time at high than at low temperatures; but the more highly diffusive the substance the less does it appear to gain by heat.

1485. *Diffusion of crystalloids through colloids.*—If the solid hydrate (jelly) of some colloid body be employed, instead of pure water, for the crystalloids to diffuse in, Mr. Graham found that the diffusion of the crystalloids proceeded through a firm jelly with little or no abatement of velocity; he took, for instance, 10 gram. of chloride of sodium and 2 gram. of the Japanese gelatine, or gelose of Payen; they were dissolved together in so much hot water as to form 100 cub. cents. of fluid. The jelly mixture was introduced into the empty diffusion jar and allowed to cool; it set into a firm jelly, occupying the lower part of the jar, and containing, of course, 10 per cent. of chloride of sodium. Instead of placing pure water over this jelly, it was covered by 700 cub. cents. of a solution containing 2 per cent. of the same gelose, cooled so far as to be on the point of gelatinizing, the jar at the same time being placed in a cooling mixture, in order to expedite that change. The jar with its contents were then left undisturbed for 8 days at the temperature 10° C. After the lapse of this time the jelly was removed from the jar in successive portions of 50 cub. cents. each from the top, and the proportion of chloride of sodium in the various strata ascertained. The results were very similar to those obtained in diffusing the same salt in a jar of pure water. The diffusion in the gelose appeared more advanced in 8 days than diffusion in water for 7 days, as will be seen by comparing the following table (XII.) with Table VIII.

TABLE XII.—*Diffusion of a* 10 *per cent. solution of chloride of sodium in the jelly of gelose, for* 8 *days, at* 10°.

Number of stratum.	Diffusate, in grams.
1	·015
2	·015
3	·026
4	·035
5	·082
6	·130
7	·212
8	·350
9	·486
10	·630
11	·996
12	1·172
13	1·190
14	1·203
15 and 16	3·450

1486. With a coloured crystalloid, such as bichromate of potash, the gradual elevation of the salt to the top of the jar is beautifully illustrated. The diffusion of a salt into the solid jelly may be considered as cementation, Mr. Graham observes, in its most active form. If, in place of a crystalloid, we substitute a colloid to diffuse through the jelly, we shall see, if caramel or other coloured colloid be employed, that the diffusion will scarcely have commenced at the end of 8 days.

1487. Gelose is not the only colloid which is permeable to crystalloids; the jelly of starch, that of animal mucus, of pectin, and other solid colloidal hydrates, all of which are, strictly speaking, insoluble in cold water, are permeable when in mass, as water is, by the more highly diffusive class of substances. But such jellies greatly resist the passage of the less diffusive substances, and cut off entirely other colloid substances like themselves that may be in solution. They resemble animal membrane in this respect. A mere film of jelly has the separating effect, as is illustrated by the following simple experiment, made by Mr. Graham.

1488. A sheet of very thin and well-sized letter paper, of French manufacture, having no porosity, was first thoroughly wetted, and then laid upon the surface of water contained in a small basin, of less diameter than the width of the paper, and the latter depressed in the centre, so as to form a tray or cavity capable of holding a liquid. The liquid placed upon the paper was a mixed solution of cane sugar and gum arabic, containing 5 per cent. of each substance. The pure water below and the mixed solution above were therefore separated only by the thickness of the wet sized paper. After 24 hours the upper liquid appeared to have increased sensibly in volume, through the agency of osmose. The water below was found now to contain three-fourths of the whole sugar, in a condition so pure as to crystallize when the liquid was evaporated on a water bath. Indeed, the liquid of the basin was only in the slightest degree disturbed by subacetate of lead; showing the absence of all but a trace of gum. Paper of the description used is sized by means of starch. The film of gelatinous starch in the wetted paper has presented no obstacle to the passage of the crystalloid sugar but has resisted the passage of the colloid gum. Mr. Graham believes the following to be the mode in which this takes place:—

1489. The sized paper has no power to act as a filter. It is mechanically impenetrable, and denies a passage to the mixed fluid as a whole. Molecules only permeate this septum, and not masses. The molecules also are moved by the force of diffusion; but the water of the gelatinous starch is not directly available as a medium for the diffusion of either the sugar or gum, being in a state of true chemical combination, feeble although the union of water with starch may be. The hydrated compound itself is solid, and also insoluble. Sugar, however, with all other crystalloids, can separate water, molecule after molecule, from any hydrated colloid, such as starch. The sugar thus obtains the liquid medium required for diffusion, and makes its way through the gelatinous septum. Gum, on the other hand, possessing as a colloid an affinity for water of the most feeble description, is unable to separate that liquid from the gelatinous starch, and so fails to open the door for its own passage outwards by diffusion. By means, therefore, of a colloidal septum, crystalloids can be separated from colloids by diffusion.

1490. The separation described is somewhat analogous to that observed in a soap-bubble inflated with a gaseous mixture composed of carbonic acid and hydrogen. Neither gas, as such, can penetrate the water film; but the carbonic acid, being soluble in water, is condensed and dissolved by the water film, and so is enabled to pass outwards and reach the atmosphere; while hydrogen, being insoluble in water, or nearly so, is retained behind within the vesicle.

1491. Mr. Graham has designated by the term dialysis the separation by diffusion through a septum of gelatinous matter. The most suitable substance for the dialytic septum Mr. Graham finds to be the material known as paper parchment, which is manufactured by Messrs. De la Rue. The apparatus used in the process is called a Dialyser, and is made by stretching a piece of the wetted paper parchment, which has been soaked for about a minute in distilled water, evenly over a hoop made of wood,—or, better, of gutta percha,—of about 2 inches in depth, and of any convenient diameter, such as 6, 8, or 10 inches, so as to form a vessel like a sieve in form (Fig. 36). The parchment is secured to the hoop by string—or, better, by a second or outer hoop—which keeps it in its place, and allows of its being removed and changed when necessary. The paper parchment should be large enough to come up to the upper edge of the hoop, so that the liquid may be prevented from passing between them. There must be no small holes in the paper parchment. To ascertain this, put some distilled water in the dialyser, to the depth of a quarter of an inch, and then place the dialyser on some white blotting paper. If any wet or dark spots appear, they indicate the existence of small holes. To close such holes, apply to the under surface of the paper about the holes some liquid albumen, put on a small patch of paper parchment, and iron the patch with a hot smooth iron. This coagulates the albumen, fixes the patch, and closes the hole.

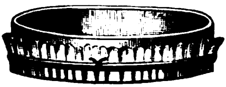

FIG. 36.

1492. The dialyser being prepared, the liquid to be dialysed is poured into it, to the depth of not more than half an inch, and the dialyser is then to be floated on distilled water contained in a flat basin (Fig. 37). The volume of water in the basin should be from 5 to 10 times greater than the volume of the fluid placed

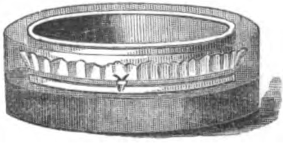

FIG. 37.

in the dialyser. The liquid is then left to dialyse for about 24 hours. A much less volume of external water suffices, provided it is changed at intervals of a few hours. The apparatus may, of course, be varied in a variety of ways. The paper parchment and other septums are suitable only for aqueous solutions; a septum suitable for dialysing alcoholic or etherial solutions has yet to be discovered.

1493. A dialyser of 6 inches diameter serves to operate upon 7 or 8 fluid ounces of liquid; one of 8 inches diameter for 12 or 14 fluid ounces; one of 10 inches diameter for 20 fluid ounces; and 1 of 12 inches diameter for 30 fluid ounces. The wider the dialyser, and the greater the quantity of distilled water used in the outer basin, the more rapid and effective is the diffusion.

1494. Mr. Graham obtained the results recorded in the table with 100 cub. cents. of a solution containing 10 grammes of each of the various substances. The area of the paper parchment septum was 0·005 square metre, and the depth of the stratum of fluid placed upon it 20 millimetres. The substances diffused were all crystalloids, with the exception of gum arabic.

TABLE XIII.—*Dialysis through parchment paper during 24 hours, at* 10° *to* 15° C.

Ten per cent. solutions.	Diffusate, in grams	Relative diffusate.
Gum arabic	0·029	·004
Starch sugar	2·000	·266
Cane sugar	1·607	·214
Milk sugar	1·387	·185
Mannite	2·621	·349
Glycerine	3·300	·440
Alcohol	3·570	·476
Chloride of sodium	7·500	1·000

1495. Solutions of the same substances and of the same strength were dialysed through a layer of animal mucus, taken from the stomach of a pig, 12 millimetres in thickness (10 grams. of humid mucus being spread over 0·005 square metres of surface), and placed between two discs of calico.

TABLE XIV.—*Dialysis through animal mucus during* 25 *hours, at* 10° *to* 15° C.

Ten per cent. solutions.	Diffusate, in grams.	Proportional diffusate.
Gum arabic - - -	·023	·004
Starch sugar - -	1·821	·360
Cane sugar - - -	1·753	·347
Milk sugar - - -	1·328	·262
Mannite - - -	1·895	·375
Alcohol - - -	2·900	·573
Glycerine - - -	2·554	·505
Chloride of sodium -	5·054	1·000

The relative diffusibilities of the different substances present a considerable degree of similarity in the two tables, and are equally analogous to the diffusibilities of the same substances observed in pure water; the intervention of a colloid septum not having impeded much the diffusion of any of these substances except the colloid gum.

1496. **Salts appear to** preserve their usual relative diffusibility unchanged by the intervention of the septum. The same partial separation of mixed salts was observed by dialysing them as in the water jar. With a mixture, for instance, of equal parts of chlorides of potassium and sodium in the dialyser, the first tenth part of the mixture which passed through was found to consist of 59·17 per cent. of chloride of potassium, and 40·83 per cent. of chloride of sodium. Double salts, also, such as alum, and the sulphate of copper and potash, which admit of being resolved into pairs of unequally diffusive salts, were largely decomposed upon the dialyser, as they are in the water jar. The effect of heat in promoting diffusion appears, however, to be diminished in dialysis, at least with a paper parchment septum. Thus the diffusion from a 2 per cent. solution of chloride of sodium in a constant period of 3 hours, was—

		Ratio.
At 10° C.	0·738 gram.	1
At 20	0·794 „	1·07
At 30	0·892 „	1·20
At 40	1·017 „	1·37

The rate of diffusion in water alone, without the septum, would have been doubled by an equal rise of temperature, instead of being increased one-third only, as above.

1497. If it is desirable to have a constant flow of water passing over the lower surface of the septum of the dialyser, so as to offer as little obstruction as possible to diffusion, the following apparatus (Fig. 38), devised by Dr. Redwood, will be found convenient. It consists of a receiver, A, which is represented standing on a block of wood, B, and over the mouth of the receiver is placed a flat-bottomed, shallow dish, C, with a central tube passing into the neck of the receiver, and having on its bottom a grooved plate of gutta percha, shown in the separate figure X. The depth of the groove in this plate is about one-eighth of an inch, and through this the water runs in a

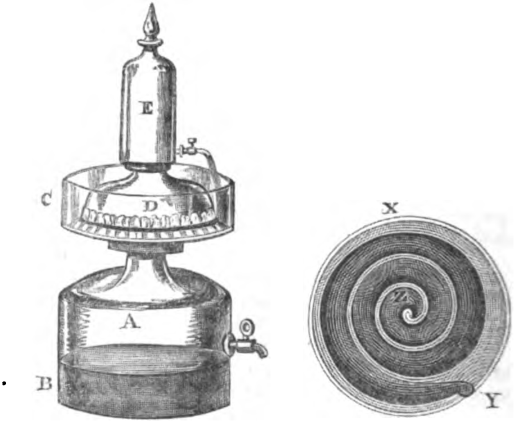

Fig. 38.

continuous stream from Y, passing off at Z through a small tube into the receiver. The dialyser, D, rests on the grooved plate, the water which fills the groove being in contact with the lower surface of the septum. E is a bottle, from which the water runs through the small stopcock and tube into the grooved plate. Instead of the grooved plate of gutta percha, the groove might be made in the bottom of the dish itself.

1498. Before entering upon the application of dialysis, we must refer again to the radical distinction which, Mr. Graham believes, exists between colloids and crystalloids, both as regards their molecular constitution and their chemical properties. Every physical and chemical property is characteristically modified in each class. They appear like different worlds of matter, and give occasion to a corresponding division of chemical science. The distinction between these kinds of matter is that subsisting between the material of a mineral and the material of an organized mass. The hardness of the crystalloid, with its crystalline planes and angles, is replaced in the colloid by a degree of softness, with more or less of rounded outline. This peculiar structure of the colloids, with their chemical indifference, appear to be required in substances that can intervene in the organic processes of life; the plastic elements of the animal body are consequently members of this class. The water of crystallization in the crystalloids is represented by the water of gelatination in the colloids. The water in gelatinous hydrates is aptly described by M. Chevreul as retained by "capillary affinity," that is, by an attraction partaking both of the physical and chemical character. While Mr. Graham admits that chemical affinity of the lowest degree may shade into capillary attraction, he believes that the character of gelatinous hydration is as truly chemical as that of crystalline hydration.

1499. Gelatinous hydrates always exhibit a certain tendency to aggregation, as is seen in the jelly of hydrated silicic acid and alumina. With some the jelly is also adhesive, as in glue and mucus. But unless they be soluble in water, gelatinous hydrates, when once formed, are not in general adhesive. Separated masses do not reunite when brought into contact. This want of adhesiveness is very remarkable in the gelose of Payen, which resembles gelatine so closely in other respects. Layers of a gelose solution, allowed to cool and gelatinize in succession, in a diffusion jar, do not adhere together.

1500. The colloidal character is not obliterated by liquefaction, and is therefore more than a modification of the physical condition of the solid. Some colloids are soluble in water, as gelatine and gum arabic; and some are insoluble, like gum tragacanth. Some colloids, again, form solid compounds with water, as gelatine and gum tragacanth; while others, like tannin, do not. In such points the colloids exhibit as great a diversity of property as the crystalloids. A certain parallelism is maintained between the two classes, notwithstanding their differences.

1501. The phenomena of the solution of a salt or crystalloid probably all appear in the solution of a colloid, but greatly reduced in degree. The process becomes slow; time, indeed, appearing essential to all colloidal changes. The change of temperature usually occurring in the act of solution becomes barely perceptible. We have already noticed that the solution is viscous or gummy, that the colloid is retained in solution by a feeble force, and that they are generally precipitated by adding to their solution any crystalloid. Of all the properties of liquid colloids, their slow diffusion in water, and their arrest by colloidal septa, are the most serviceable in distinguishing them from the crystalloids.

1502. Soluble crystalloids are always highly sapid; soluble colloids are singularly insipid. It is doubtful whether a colloid, when tasted, ever reaches the sentient extremities of the nerves of the palate, as the latter are probably protected by a colloidal membrane impermeable to soluble substances of the same physical constitution. It has been observed that vegetable gum is not digested in the stomach. The coats of that organ dialyse the soluble food, absorbing crystalloids and rejecting all colloids. This action appears to be aided by the thick coating of mucus which usually lines the stomach.

1503. The secretion of free hydrochloric acid during digestion, at times most abundant, appears to depend upon processes of which no distinct conception has been formed; but certain colloidal decompositions are equally inexplicable upon ordinary chemical views. To facilitate the separation of hydrochloric acid from the perchloride of iron, for instance, that salt is first rendered basic by the addition of peroxide of iron. The comparatively stable perchloride of iron is transformed by such treatment into a feebly-constituted colloidal hydrochlorate. The latter compound breaks up, under the purely physical agency of diffusion, and divides on the dialyser into colloidal peroxide of iron and free hydrochloric acid. The superinduction of the colloidal condition may possibly form a stage in many analogous organic decompositions.

1504. Although colloids can generally be precipitated from their aqueous solution by the addition of any crystalloids, and likewise that any of the latter class can decompose the solid hydrates of the former by taking away the water, nevertheless, anhydrous colloids can decompose certain crystalloid hydrates. The water in alcohol of greater strength than corresponds with the density 0·926, which represents the definite hydrate $C_4H_6O_2 + 6HO$, is certainly in a state of chemical union; but alcohol so high as 0·906, contained in a close vessel, is concentrated in a notable degree by contact with dry mucus, gelatine, and gum, and sensibly even by dry parchment paper. Dilute alcohol, divided from the air of the atmosphere by a dry septum of mucus, gelatine, or gum, is also concentrated by evaporation, as in the well-known bladder experiment of Sömmering, The selective power is here apparent of the colloid for water, that fluid being separated from alcohol, and travelling through the colloidal septum by combination with successive molecules of the latter, till the outer surface is reached, and evaporation takes place. The penetration in this manner of a colloid by a foreign substance may be taken as an illustration of the phenomena of cementation. Iron, and other substances which soften under heat, may be supposed to assume at the same time a colloidal constitution; so it may be supposed does silica, when fused into a glass by heat, and every other vitreous substance.

1505. As regards chemical properties, the crystalloidal appears the energetic form, and the colloidal the inert form of matter. In their capacity as acids and bases, the colloids are very inert. When in union with a crystalloid, they are united with only a feeble force, even if the crystalloid be a powerful reagent of its own class, such as an acid or an alkali. The equivalent of a colloid appears to be always high, although the ratio between the elements of the substance may be simple. Gummic acid, for instance, may be represented by $C_{12} H_{11} O_{11}$; but, judging from the small proportions of lime and potash which suffice to neutralize this acid, the true numbers of its formula must be several times greater. Mr. Graham remarks, "It is difficult to avoid associating the inertness of colloids with their high equivalents, particularly when the high number appears to be attained by the repetition of a smaller number. The inquiry suggests itself, whether the colloid molecule may not be constituted by the grouping together of a number of smaller crystalloid molecules, and whether the basis of colloidality may not really be this composite character of the molecule."

1506. Silicic acid can exist both as a crystalloid and a colloid. Mr. Graham has designated it in its latter state, co-silicic acid. The equivalent of co-silicic acid appears to be 36 times greater than the silicic acid in its crystalloid state. The apparently small proportion of acid in a variety of metallic salts, such as certain red salts of iron, is accounted for by the high colloidal equivalent of their bases. The effect of such an insoluble colloid as Prussian blue in carrying down small proportions of the precipitating salts, may admit of a similar explanation.

1507. Gelatine appears to hold an important place as a colloidal base. This base unites with colloidal acids, giving a class of stable compounds, of which tanno-gelatine only appears to be hitherto known. Gelatine is precipitated entirely by a solution of metaphosphoric acid, added drop by drop, 100 parts of gelatine uniting with 3·6 parts of the acid. The compound formed is a semi-transparent, soft, elastic, and stringy solid mass, presenting a startling resemblance to animal fibrin. It will be an interesting inquiry, Mr. Graham remarks, whether metaphosphoric acid is a colloid, and enters into the compound described in that character, or is a crystalloid, as the small proportion and low equivalent of the acid would suggest.

1508. Although chemically inert in the ordinary sense, colloids are eminently characterised by the quality of *mutability*. Their existence is a continued metastasis. A colloid may be compared in this respect to water, while existing liquid, at a temperature under its usual freezing point, or to a supersaturated saline solution. Fluid colloids appear to have always a *pectous*[*] modification. They become pectous and insoluble by contact with certain other substances, without combining with these substances, and often under the influence of time alone. The pectizing substance appears to hasten merely an impending change. Even while fluid a colloid may alter sensibly, from colourless becoming opalescent; and while pectous the degree of hydration may become reduced from internal change. The gradual progress of alteration in the colloid effected by the agency of time is an investigation yet to be entered upon. The solution of co-silicic acid, for example, cannot be preserved; it may remain fluid for days or weeks in a sealed tube, but is sure to gelatinize and become insoluble at last. Nor does the change of this colloid appear to stop at that point; for the mineral forms of silicic acid deposited from water, such as flint, are often found to have passed, during the geological ages of their existence, from the vitreous, or colloidal, into the crystalline condition. The colloidal is, in fact, a *dynamical* state of matter; the crystalloidal being the *statical* condition. The colloid possesses ENERGIA. It may be looked upon as the probable primary source of the force appearing in the phenomena of vitality. To the gradual manner in which colloidal changes take place (for they always demand time as an element) may the characteristic protraction of chemico-organic changes also be referred.

1509. We must preface our description of the curious and extraordinary state in which a number of colloid bodies have been obtained by Mr. Graham by means of dialysis, by describing the interesting discovery which Mr. W. Crum made some years ago, viz., that there is a form of alumina which is *soluble* in water. He found in his investigation of the aluminous compounds and their properties, that there are two binacetates of alumina; one is soluble in water; the other, which may be considered an allotropic binacetate, is insoluble. When a dilute solution of the soluble binacetate is exposed to heat for some days, the whole, or nearly the whole, of the acetic acid becomes free, and is expelled by the heat, and the alumina, which is thus set free, *is soluble and remains in solution;* and it is instantly coagulated on adding to its solution a minute quantity of a mineral or vegetable acid, or one of the alkalies; it is also coagulated by a great number of salts, and by decoctions of dye-woods. A solution of this alumina, containing only $\frac{1}{4}$ *per cent.* of alumina, is converted into a solid transparent jelly when mixed with half its bulk of water acidulated with $\frac{1}{2500}$ of sulphuric acid. The jelly has, therefore, only $\frac{1}{600}$ of its weight of alumina, and $\frac{1}{7500}$ of sulphuric acid. The coagulated alumina is insoluble in any acid, whether cold or hot, as well as in pure water; it dissolves, however, in a boiling solution of potash or soda, and when the alkaline solution is afterwards saturated, the ordinary terhydrate of alumina is precipitated. As regards the alumina in its soluble form, we may add that it is incapable of acting as a mordant, and it is also incapable of entering into any other definite combination.*

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[*] From a Greek word signifying *curdled*, as fibrin, casein, albumen; but certain liquid colloid substances are capable of forming a jelly, and yet still remain liquefiable by heat and soluble in water. Such is gelatine itself, which is not pectous in the condition of animal jelly, but may be so as it exists in the gelatinous tissues.

1510. The sesquioxide of iron, the sesquioxide of chromium, alumina, &c., when added in their hydrated state to a solution of their salts of the monobasic acids, such as hydrochloric and nitric, will dissolve in large quantities in these solutions in the course of time: the solution demands time; the quantity of the oxide taken up will therefore go on increasing for a long time, if digestion in the cold is continued. Mr. Ordway found sesquichloride of iron to take up so much as 18 equivalents of peroxide of iron in the course of 5 months. Now these basic salts are *colloidal* bodies, and the neutral salts are crystalloidal. If solutions of the neutral salts are placed in the dialyser the salts diffuse away without decomposition; but if the collodial salts (the basic salts) are placed in the dialyser, the acid diffuses away, and the base is left, but in such a curious state that it is soluble in water, and is coagulated on the addition of foreign matter to its solution.

1511. Sulphuric and other polybasic acids give insoluble subsalts with excess of ferric oxide, or any other aluminous oxide, and therefore they cannot be employed for these solutions of the oxides.

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* *Chemical Society's Quarterly Journal* vi., 216.

1512. Mr. Graham dialysed a solution of alumina in chloride of aluminum, consisting at first of 52 parts of alumina to 48 of hydrochloric acid: after a dialysis of 6 days, it contained 66·5 per cent. of alumina; after 11 days, 76·5 per cent.; after 17 days, 92·4 per cent.; and after 25 days the alumina appeared to be as nearly as possible free from acid, as traces only of hydrochloric acid were indicated by an acid solution of nitrate of silver. But in such experiments the alumina often pectizes in the dialyser before the hydrochloric acid has entirely escaped.

1513. Acetate of alumina with an excess of alumina gave similar results. The alumina remained fluid in the dialyser for 21 days, and when it pectized was found to retain 3·4 per cent. of acetic acid, which is in the proportion of 1 equivalent of acid to 28·2 equivalents of alumina.

1514. Soluble alumina is one of the most unstable of substances, a circumstance which fully accounts for the difficulty of preparing it in a state of purity. It is coagulated or pectized by portions so minute as to be scarcely appreciable of sulphate of potash, and, Mr. Graham believes, by all other salts, and also by ammonia. A solution containing 2 or 3 per cent. of alumina was coagulated by a few drops of well-water, and could not be transferred from one glass to another, unless the glass was repeatedly washed out by distilled water, without gelatinizing. Acids in small quantities also cause coagulation; but the precipitated alumina readily dissolves in excess of acid, showing that it is not the same form of soluble alumina which Mr. Crum discovered. There are, as we shall see more at length presently, two soluble modifications of alumina,—alumina, which is the one we are at present describing; Mr. Crum's alumina, which is termed "metalumina."

1515. The colloids gum and caramel precipitate this alumina. It is also a mordant, and in fact possesses all the properties of the base of alum and the ordinary aluminous salts. A solution containing 0·5 per cent. of alumina may be boiled without gelatinizing, but when concentrated to half its bulk, it suddenly coagulates. Soluble alumina gelatinizes when placed upon red litmus paper, and forms a faint blue ring about the drop, showing a feeble alkaline reaction. Soluble alumina is not precipitated by alcohol nor by sugar. No pure solution of alumina, although dilute, remains fluid for more than a few days. Colloid alumina, we see then, may exist either fluid or pectous; in other words, it has a soluble and an insoluble form, the latter being the gelatinous alumina, as precipitated by bases. It is evident that the extraordinary coagulating action of salts upon hydrated alumina must prevent the latter substance from ever appearing in a soluble state when liberated from combination by means of a base.

1516. Colloidal alumina possesses also a high atomic weight, like co-silicic acid. The chloride of alumina, with excess of alumina, is a colloidal hydrochlorate of alumina, containing the latter substance, with its large colloidal equivalent, and may be really neutral in composition. The soluble basic persalts of iron, tin, &c., are likewise all colloidal, and have, no doubt, a similar composition. Such colloidal salts, we have already noticed, are themselves slowly decomposed on the dialyser, being resolved into the crystalloidal acid, which escapes, and the colloidal oxide, which remains behind.

1517. The metalumina of Mr. Crum can be obtained by dialysing a solution of acetate of alumina which has been altered by heat. In 3 days the acetic acid was reduced on the dialyser to 11 per cent., giving 1 equivalent of acetic acid to 8 equivalents of alumina; in 6 days, to 7·17 per cent. acid; in 13 days, to 2·8 per cent. acid, or 1 equivalent of acid to 33 equivalents of alumina. The solution of metalumina is tasteless, and, according to Mr. Graham's observations, entirely neutral to test-paper. Metalumina, we have noticed, is coagulated by acids, &c.; like alumina, therefore, it has a fluid and pectous form.

1518. Soluble peroxide of iron and soluble metaperoxide can also be prepared in a similar way, and they have each a pectous form.

1519. Ferrocyanide of copper dissolves in a solution of oxalate of ammonia; if this solution is dialysed, the oxalate of ammonia diffuses away, and ferrocyanide of copper is left in a state which renders it soluble in water.

1520. By dissolving Prussian blue in a solution of oxalic acid, and dialysing the solution, the oxalic acid diffuses out, and the Prussian blue which is left is soluble in water.

1521. Pure silica, in solution in water, can be obtained by the aid of dialysis, and this solution may be made to contain as much as 14 per cent. of silica. This solution of silica, however, is unstable, especially when it contains the quantity of silica named. It rarely remains fluid for more than a few days, the silica then separating in the gelatinous state. If the solution be diluted, it keeps better, but in either case the coagulation of the silica is effected by the addition of a small quantity, even $\frac{1}{10000}$ part of an alkaline or earthy carbonate, but not by caustic ammonia.

1522. Mr. Graham was unable at first to obtain stannic acid, the analogue of silicic acid, in the soluble colloidal form; he could only get it in the pectous state. Precipitated peroxide of tin, though insoluble in water, is readily soluble in a solution of bichloride of tin. When the liquid so produced is dialysed, the whole of the chlorine passes away, but a jelly, instead of a solution, is left on the dialyser. Mr. Graham afterwards found that by acting upon this jelly with a dilute alkali, and then submitting it to a further dialysis, it gradually becomes liquid. This last process he terms peptizing, or digesting. The soluble co-stannic acid is very readily pectized.

1523. We have learned, then, that the hydrated peroxides of the aluminous type, when free, are colloid bodies; that two species of each of these hydrated oxides exist, of which alumina and metalumina are the types, one derived from an unchanged salt, and the other from the heated acetate of the base; further, that each of these species has two forms, one soluble and the other insoluble, or coagulated. The possession of a soluble and an insoluble (fluid and pectous) modification is not confined to hydrated silicic acid and the aluminous oxides, but appears to be very general, if not universal, among colloid substances. The double form is typified in the fibrin of the blood.

1524. Organic colloidal substances can, like the mineral colloids, be obtained pure, and in the soluble or pectous state by the aid of dialysis.

1525. Albumen, in the purest state in which it is presented in nature, namely, in the white of egg, contains a portion of soda, which gives it a faint alkaline reaction, and to which its solubility is sometimes ascribed. By mixing the egg albumen with acetic acid, and placing the mixture on the dialyser, all the acid with the alkaline and earthy salts diffuse away, and leave the albumen pure, so that, when burnt, it leaves no ash. This purified albumen still retains its constituent sulphur. It has a faint acid reaction.

1526. Gum, as represented by the best gum arabic, has been shown by Frémy to be a compound of an organic acid, gummic acid, and lime. The lime present in this compound constitutes rather less than 2 per cent. of the gum; it may be partially removed by oxalic acid, but is completely removed, and with facility, by dialysis. If 4 or 5 per cent. of hydrochloric acid be added to a 20 percent. solution of gum, and the mixture placed on the dialyser, the hydrochloric acid and lime will diffuse out, leaving the gummic acid in solution. If this be evaporated to dryness, and heated for some hours at 212° F., it becomes insoluble in water, and merely swells up into a gelatinous mass, like gum tragacanth.

1527. Other colloidal organic substances, as tannin and caramel, may be obtained from crystalloids in like manner.

1528. *Separation of poisons from colloidal liquids.*—Dialysis may be advantageously applied to the separation of poisons, whether organic or inorganic, from organic solutions, in medico-legal inquiries; for all soluble poisonous substances, whatever their origin, appear to be crystalloids, and will accordingly pass through colloidal septa. The process has the advantage of introducing no metallic substance or chemical reagent of any kind into the organic fluid. The arrangement for operating is also of the simplest nature.

1529. *Osmose.*—Closely connected with dialysis is the phenomenon originally termed endosmose and exosmose. Dutrochet observed, long ago, that whenever two liquids of different densities, capable of being mixed with each other, are separated by a membranous partition, two currents become established, one from within to without (exosmose,—εξ, and ωσμος, impulse), and another in the contrary direction (endosmose,—ενδον, inwards, and ωσμος); these terms are now seldom employed, the shorter term osmose, which includes the two, being substituted.

1530. If in the opening of a membranous bag or bladder a long glass tube is fastened hermetically, we have an osmometer. If the bladder be filled with a concentrated solution of common salt, and then suspended in a jar of pure water, the salt will of course diffuse out into the water; but at the same time a quantity of water diffuses into the bladder; and the remarkable fact connected with the experiment is this, that the volume of water which enters the bladder is very much greater than could be introduced by simple liquid diffusion, amounting in some cases to several hundred times that of the salt displaced; the liquid rises in the glass tube, attaining in some cases a very considerable height. The movement of the salt can be explained by diffusion; it is the flow of water which is the important phenomenon. The flow of liquid takes place generally, though not always, from the water to the saline solution, so that the quantity diminishes on one side of the septum while it increases on the other. The volume of water which passes through the septum varies with different liquids. In general, endosmose takes place towards the denser liquid. Alcohol and ether form an exception to this; they behave like liquids which are denser than water.

1531. The subject has been carefully examined by Mr. Graham, who has established several important facts in relation to it. He used as septa in his osmometer, which was constructed in a peculiar way, fresh ox-bladder, or a piece of cotton cloth soaked in white of egg and dipped into boiling water to coagulate it, and also the porous earthenware cells of a galvanic battery. He found, first, that solutions of neutral organic substances, such as urea, gum arabic, and sugar of milk, caused little or no osmotic action; secondly, that neutral salts, such as sulphate of magnesia, chloride of sodium, and chloride of barium, likewise produced but little effect; thirdly, that alkaline solutions, and especially solutions of the carbonates of potash and soda, caused a very rapid flow of the water. For example, when a solution of carbonate of potash was placed in the osmometer, containing 1 part of salt to 1,000 of water, 500 grains of water entered the instrument to every grain of the salt diffused into the outer cylinder, and it was generally found that osmose was most rapid when the solution did not contain more than 2 per cent.

of the salt; fourthly, that acid solutions, either dilute acids or acid salts, caused a current in the opposite direction to that caused by the alkaline solution; lastly, that the corrosion of the septum seemed to be a necessary condition of osmose, the water always flowing to the alkaline side. When septa were used which were not chemically acted upon by the saline solution, there appeared to be no osmotic action, although they were not deficient in porosity.

1532. Many theories have been proposed to account for osmose, but we shall only notice what Mr. Graham states with regard to it at the close of his paper on dialysis. He considers it to be an affair of hydration and of dehydration in the substance of the membrane or other colloid septum, and that the diffusion of the saline solution placed within the osmometer has little or nothing to do with the osmotic result, otherwise than as it affects the state of hydration of the septum.

1533. Osmose is generally considerable, through membranous and other highly hydrated septa, with the solution of any colloid (gum, for instance) contained in the osmometer. Yet the diffusion outwards of the colloid is always minute, and may sometimes amount to nothing. Indeed, an insoluble colloid, such as gum tragacanth, placed in powder within the osmometer, was found to indicate the rapid entrance of water, to convert the gum into a bulky gelatinous hydrate. Here no outward or double movement is possible.

1534. The degree of hydration of any gelatinous body is much affected by the liquid medium in which it is placed. This is very obvious in fibrine and animal membrane. Placed in pure water, such colloids are hydrated to a higher degree than they are in neutral saline solutions. Hence the equilibrium of hydration is different on the two sides of the membrane of an osmometer. The outer surface of the membrane, being in contact with pure water, tends to hydrate itself in a higher degree than the inner surface does, the latter surface being supposed to be in contact with a saline solution. When the full hydration of the outer surface extends through the thickness of the membrane, and reaches the inner surface, it there receives a check. The degree of hydration is lowered, water must be given up by the inner layer of the membrane, and it forms the osmose. The contact of the saline fluid is thus attended by a continued catalysis of the gelatinous hydrate, by which it is resolved into a lower gelatinous hydrate and free water. The inner surface of the membrane of the osmometer contracts by contact with the saline solution, while the outer surface dilates by contact with pure water. Far from promoting this separation of water, the diffusion of the salt throughout the substance of the membrane appears to impede osmose, by equalizing the condition, as to saline matter, of the membrane through its whole thickness. The advantage which colloidal solutions have in inducing osmose appears to depend in part upon the low diffusibility of such solutions, and their want of power to penetrate the colloidal septum.

1535. The substances fibrine, albumen, and animal membrane swell greatly when immersed in water containing minute proportions of acid and alkali. On the other hand, when the proportion of acid or alkali is carried beyond a point peculiar to each substance, contraction of the colloid takes place. Such colloids as have been named acquire the power of combining with an increased proportion of water, and of forming superior gelatinous hydrates, in consequence of contact with dilute acid and alkaline reagents. Even parchment paper is more elongated in an alkaline solution than in pure water. When so hydrated and dilated, the colloids present an extreme osmotic sensibility. Used as septa, they appear to assume or resign their water of gelatination under influences apparently the most feeble. Mr. Graham says he does not attempt to explain this varying hydration of colloids with the osmotic effects thence arising. Such phenomena belong to colloidal chemistry, where the prevailing changes in composition appear to be of the kind vaguely described as catalytic. To the future investigation of catalytic affinity, therefore, must we look, he says, for the further elucidation of osmose.

1536. There is a close connection between the subjects treated of in this chapter and the flow of liquids through capillary tubes; but we are unable to do more than refer the student to the first volume of Miller's "Chemistry," 2nd edition; and to Graham's Memoir on the subject, in the "Philosophical Transactions" for 1862.

CHAPTER XV.

ON CHEMICAL ANALYSIS BY SPECTRUM OBSERVATIONS.

Coloured flames, and their utility in chemical analysis, 1537. *Spectrum analysis*, 1539. *Spectra of the metals of the alkalies and alkaline earths*, 1540. *Description of the apparatus for spectrum analysis*, 1541. *Delicacy of the spectrum reactions of bodies*, 1543. *Increase of luminous lines with an increase of temperature*, 1545. *Do the different compounds of the same metal produce lines of the same colour?* 1546. *Do any of the lines of the different metals coincide?* 1549. *Are the lines of any substance obliterated or altered by the presence of another substance?* 1550. *Spectra of the metalloids*, 1551. *Spectra of solids and vapours contrasted*, 1552. *Relation between the absorption and emission of heat and light by bodies*, 1553. *Dark lines in the solar spectrum*, 1554. *The dark lines vary with the nature of the luminous source*, 1556. *The solar spectrum, and the spectrum of an incandescent solid or liquid contrasted*, 1557. *Chemical constitution of the sun's atmosphere*, 1558. *Chemical constitution of the atmosphere of the fixed stars*, 1559. *Appendix N.: Arrangement of the spectrum apparatus*, 1560.

1537. *Coloured flames, and their utility in chemical analysis.*—The different metals, when in an intensely heated and vaporized state, produce different coloured flames; and as the compounds of the alkaline metals are readily volatilized in a gas or spirit flame, chemists have long employed the colours they impart to the flame as a test of their presence; but as the coloured flame produced by one metal obscures that given by another, the application of coloured flames to analysis was, on this account, very limited. Thus, as the yellow colour produced by a sodium compound conceals the violet produced by a potassium one, it became necessary, when the former was present, to adopt other methods of analysis to prove the presence or absence of the latter.

1538. The application of coloured flames to analysis was extended by Cartmell. He proposed that after any compound of a metal, the colour of which can be seen by the naked eye, and which conceals the colours which the other metals, which might be associated with it, impart, had been detected, that the flame should be viewed, for the purpose of detecting the other substances, if present, through coloured glasses or liquids, which would absorb the rays of the body already detected, whilst they would transmit the rays of the metals which remained undetected. Thus, in examining for sodium and potassium compounds, if the flame were coloured yellow, proving the presence of a compound of the former metal, he proposed that the flame should then be viewed through a piece of glass stained blue with cobalt, in order to ascertain whether a potassium compound was present. The yellow rays produced by sodium are absorbed by the blue glass, whilst the violet rays produced by potassium are transmitted, and thus, by the aid of the blue glass, a potassium compound can, in the presence of a sodium compound, be detected by the colour it imparts to the flame, which was before impossible.

1539. *Spectrum analysis.*—If the coloured flame produced by metals in the vaporized state be transmitted through a PRISM, instead of coloured glasses or coloured liquids, the different colours imparted to the flame become as completely separated as the colours composing white light are by the same means; for a ray of white light, when transmitted through a flint glass prism, is not only refracted and bent out of its path in passing through this medium, but also, instead of there being one colourless spot of light upon the screen behind, there is a series of coloured spots, or rather bands, overlapping each other. At the upper part of this image (or *spectrum*, as it is called) will be the most refrangible, and at the lower part the least refrangible ray; the colour of the upper or most refrangible one will be *violet*, and the lower, or least refrangible one will be *red;* the intermediate ones, commencing from the violet end, being *indigo*, *blue*, *green*, *yellow*, and *orange*, all graduating imperceptibly into each other. The spectrum of solar light furnishes all the primary colours, commencing at red and terminating in violet; and there are no *wide gaps* between the different colours, they imperceptibly merge into each other. This is not the case with the spectrum furnished by a vaporized metal. It consists of a series of bright bands of particular colours, separated by dark bands of varying width. The student will see that, owing to the fact that none of the metals yield a spectrum composed of all the primary colours, but that each metal yields differently coloured bands of different refrangibility, it becomes possible to detect each individual in a mixture of metals, as the bands of light furnished by each differ, not only in colour, but occupy, from their unequal refrangibility, different positions in the spectrum. Even when two or more metals yield bands of the same colour, the bands furnished by these metals differ in intensity of colour, in breadth, in number, and in the position they occupy in the spectrum. The colours from the vaporized metals occupy the same position in the spectrum as the corresponding colours from white light.

1540. *Spectra of the metals of the alkalies and alkaline earths.*—When compounds of the alkalies and alkaline earths are introduced into a Bunsen's burner, and the flame is viewed through a spectrum apparatus, the metals in the metallic compounds are found to give the following spectra:—Sodium gives a yellow line,* in a position corresponding to the yellow rays of the solar spectrum; potassium gives a continuous spectrum in the centre, a red line in the extreme red rays, and a violet line in the extreme violet rays; lithium gives two sharply defined lines,—a pale yellow, corresponding to the yellow rays, and a bright red, corresponding to the red rays; strontium gives eight characteristic lines,—six of them are red, and correspond in position to the red rays of solar light; one is orange, which is parallel to the orange rays; and the other is a blue line, in the situation of the blue rays: barium gives two green bands in the situation of the green rays, and besides these, three other green bands, and several yellow, orange, and red lines; calcium gives one green band in the situation of the yellow-green rays, and a bright orange band near the red rays, besides several smaller orange lines. Magnesium compounds are not volatilized in a Bunsen's burner, and therefore do not impart a colour to the flame at that temperature; but the magnesium spectrum can be obtained at that temperature by burning the pure metal in the flame.

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* The sodium line, when more minutely examined by a larger number of prisms, is seen to be composed of two lines.

1541. *Description of the apparatus for spectrum analysis.* —Although many scientific men had examined the spectra of different elementary bodies, it is to Kirchhoff and Bunsen that the distinguished merit is due for reducing the prismatic observation of flame tinged by the salts of the different metals to a simple and systematic method of analysis.* The latest form of instrument which they employed for this purpose is represented in Fig. 39. It consists of an iron tripod stand, A, on which a flint-glass prism, B, having a refracting angle of 60°, is placed, and which is kept in its position by a spring, *c*. At the end of the tube, D, nearest the prism, is placed a lens, and at the other end of the tube is a slit, the width of which can be regulated by the micrometer screw, *e*. The upper half of the slit is left free; in the lower half is

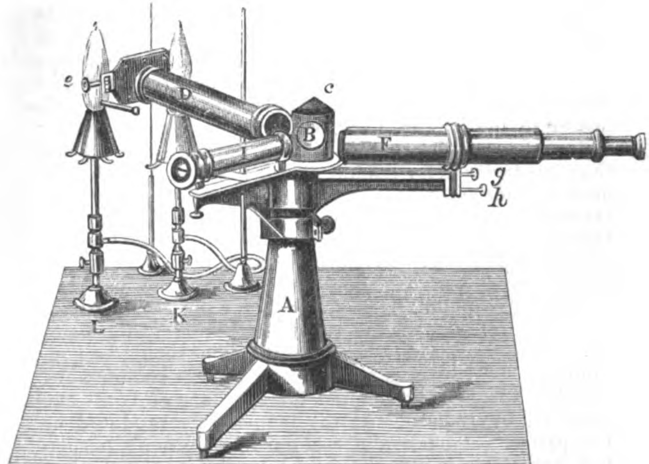

FIG. 39.

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* The student will find the history of this discovery very interesting. He will find some papers bearing on it in the *Chemical News* for 1861; and he will also find a brief but interesting account in Professor Miller's Lecture on Spectrum Analysis in the *Chemical News* for 1862.

placed a small equilateral glass prism, the use of which will presently be described. The telescope, F, which has a magnifying power of 8, is moveable in a horizontal plane around the axis of the tripod: *g* and *h* are screws for adjusting the axis of the telescope, so as to bring any part of the slit at *e* into the centre of the field of vision. The tube, I, is also moveable in a horizontal direction. This tube contains, at the end next to the prism, a lens; at the other end is a scale divided into millimetres. When the telescope has been properly adjusted to the examination of the spectrum, the tube, I, is moved until it is placed at such an angle with the telescope and the face of the prism, that when a light is transmitted through the scale, the image of this scale is reflected into the telescope from the face of the prism nearest the observer. This image is rendered perfectly distinct by pushing in the tube which holds the scale nearer to the lens in I, or withdrawing it to a greater distance, as may be required. The lines of the scale can then be employed for reading off the position of the bright or dark lines of the spectrum, as both will appear simultaneously, overlapping each other in the field of the telescope. By turning the tube, I, round upon the axis of the tripod, any particular line of the scale can be brought to coincide with any desired line of the spectrum.

1542. To examine, by means of this or any other form of spectrum apparatus,* the colours imparted to the flame by substances, it is necessary that the flame should be non-luminous. Coal gas is the most convenient combustible, and the burner best adapted for the purpose is the one invented by Bunsen. At the temperature produced by the perfect combustion of coal gas in a Bunsen's burner, the compounds of the metals of the alkalies and alkaline earths, with the exception of the magnesium compounds, are volatilized; but the spectra of the other metals are best obtained by causing a spark of a Ruhmkorff's coil to strike between the wire points of the metals under examination. Stray light must be excluded, which is effected by covering the stand, the prism, and the ends of the tubes adjoining it with a loose black cloth. The upper half of the slit, *e*, we have already stated, is left free, whilst in the lower half is placed a small glass prism, which sends, by total reflection, the light of the lamp K through the slit, whilst the rays from the lamp L, pass freely through the upper and uncovered half. A small screen placed above the prism prevents any of the light from D passing through the upper portion of the slit. By this arrangement, the observer sees the spectra of the two sources of light, the one immediately under the other, and can therefore easily determine whether the lines in the two spectra are coincident or not. We will illustrate the use of this small prism by an example. If we wanted to know, for instance, whether a substance contained lithium, we introduce a bead of a *pure lithium salt* into one flame, and a bead of the substance into the other. If we find, on looking through the telescope, that the lines of the lithium salt coincide exactly with those of the substance under examination, then we know that the latter contains lithium, as the lines from no other substances coincide with those of lithium.*

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* A spectroscope with direct vision has been recently invented by Hofmann of Paris.

1543. *Delicacy of the spectrum reaction of bodies.*— The spectrum reactions of bodies are incomparably more delicate than their chemical reactions. Bunsen and Kirchhoff estimated the sensitiveness of the reaction of some of the alkaline metals by deflagrating a given weight of the various salts in the room in which they were experimenting, and diffusing the vapour mechanically through the air; in this way they arrived at the astounding fact that $\frac{1}{180,000,000}$th part of a grain of soda and $\frac{1}{6,000,000}$th part of a grain of lithia can be easily detected. The sodium reaction is the most sensitive of all, and so extensively is common salt diffused, that the sodium lines are always found to be present in the flame. Formerly, lithia was only known to occur in four minerals, but by the aid of the spectroscope we have discovered that it is very widely distributed in minute quantities; it exists in almost all rocks, in sea and river waters, in the ashes of plants, in human blood, and muscular tissue. This new method of analysis led Bunsen to discover two new alkaline metals, *cæsium* and *rubidium*, the first named from *cæsius*, "sky-coloured," in allusion to two characteristic blue lines in its spectrum; the second from *rubidus*, "dark red," owing to the existence in its spectrum of two red lines of remarkably low refrangibility. These bases were found in the mother liquor from the Durkheim spring; every ton of the water contains about three grains of chloride of cæsium, and rather less than four grains of chloride of rubidium. These two salts so closely resemble chloride of potassium in properties, that it would have been impossible, from the minute proportion in which they occur in the water, to have ascertained their presence but for the method of spectrum analysis. A new metal, thallium, has also been discovered by Mr. Crookes by means of the spectroscope.

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* The arrangement of the instrument is described in Appendix N.

1544. If the substance to be examined is volatile at the temperature obtained in a Bunsen's gas-lamp, a small bead of it is introduced on a platinum wire into the middle part of the gas flame, and at its outer edge. The chlorides, from their greater volatility, are better adapted than any of the other salts of the alkalies and alkaline earths for spectrum purposes. Mr. Crookes recommends the use of chlorates, which, of course, decompose in the flame into chlorides and oxygen; the spectra from the chlorates are much more intense than from any other class of salts; their spectra approach that high degree of intensity hitherto only attainable by the electric spark. Lines are observed when chlorates are volatilized in the gas flame, which are not seen when the other salts are volatized. These lines we shall refer to in the next paragraph.

1545. *Increase of the luminous lines with an increase of temperature.*—The bands or lines of the metals increase in number, and alter with increase of temperature. Kirchhoff found that at the high temperature of the electric spark a number of bright lines appear in the calcium spectrum which do not appear at the temperature of the coal-gas flame; a similar discovery has been made by Dr. Tyndal with regard to the spectrum of lithium. He found that when a compound of this metal was volatilized at the temperature of the electric spark, a blue band appears in its spectrum, which is altogether invisible when the compound is volatilized in a coal-gas flame. These observations have been confirmed and extended by Professors Clinton and Roscoe. They have discovered that with increase of temperature similar changes occur in the spectra of strontium and barium; but not only have they found that new lines appear at the high temperature of the intense spark, but that the *broad bands*, characteristic of the metal or metallic compound, *at the low temperature* of the coal-gas flame, *totally disappear at the higher temperature*. The new bright lines which replace the broad bands are generally not coincident with any part of the band, sometimes being less, and sometimes more refrangible. They suggest that the broad band of the flame spectrum may be due to the vapour of *some compound*, probably the oxide, of the difficultly reducible metal; whereas the bright lines which are produced at the enormously high temperature of the intense electric spark, form the true spectrum of the metal, for at that temperature the metalline compound, which they suggest exists at a lower temperature, is decomposed. Dr. Miller has likewise found that the spectrum of the recently discovered metal, thallium, contains at the high temperature of the intense spark several lines which do not appear when the metal is volatilized at a lower temperature.*

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* "The position of the bright lines, or, to speak more precisely, the maximum of light in the spectrum of an incandescent vapour, is not dependent upon the temperature, upon the presence of other vapours, or upon any other conditions, except the chemical constitution of the vapour. Of the validity of this conclusion Bunsen and I have assured ourselves by experiments made for that special object, and I have confirmed it by many observations made with a still more delicate instrument. The appearance of the spectrum of the same vapour may, nevertheless, be very different under different circumstances. Even the alteration of the mass of the incandescent gas is sufficient to effect a change in the character of the spectrum. If the thickness of the film of vapour, whose light is being examined, be increased, the luminous intensities of all the lines increase, but in different ratios; the intensity of the bright lines increases more slowly than that of the less visible lines. The impression which a line produces on the eye depends upon its breadth as well as upon its brightness. Hence it may happen that one line being less bright, although broader, than a second, is less visible when the mass of incandescent gas is small, but becomes more distinctly seen than the second line when the thickness of the vapour is increased. Indeed, if the luminosity of the whole spectrum be so lowered that only the most striking of the lines are seen, it may happen that the spectrum appears to be totally changed, when the mass of the vapour is altered. Change of temperature appears to produce an effect similar to this alteration in the mass of the incandescent vapour. If the temperature be raised, no deviation of the maximum of light is observed, but the intensities of the lines increase so differently, that those which are most plainly seen at a high temperature are not the most visible at a low temperature. This influence of the mass, and of the temperature of the incandescent gas, explains perfectly why, in the spectra of many metals, those lines which

1546. *Do the different compounds of the same metal produce lines of the same colour?* — Bunsen and Kirchhoff compared the spectra obtained from the pure chlorides of potassium, sodium, lithium, strontium, calcium, and barium, with those produced when the bromides, iodides, hydrates, sulphates, and carbonates of the several metals were brought into the following flames:—

	Temperature of flame.
Into the flame of sulphur - - -	1,820° C.
„ „ bisulphide of carbon -	2,195
„ „ aqueous alcohol - -	
Into the non-luminous flame of coal-gas -	2,350
Into the flame of carbonic oxide - -	3,042
„ „ hydrogen (in air) - -	3,259
Into the oxyhydrogen flame - - -	8,061

1547. These experiments led them to the conclusion that neither the alteration of the bodies with which the several metals may be combined, nor the variety of the chemical processes occurring in the several flames, nor the wide differences of temperature which these flames exhibit, *produce any effect upon the position of the bright lines in the spectrum which are characteristic of each metal.*

1548. This conclusion must now be received with some limitations, at least as regards difference of temperature, for more recent experiments have shown, as we have noticed in the preceding paragraph, that with increase of temperature new lines appear in the spectra, and that the bands that are produced at a low temperature are replaced, at a high temperature, by lines which are not

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are the most prominent when the metal is placed in the gas-flame, are not the most distinct when the spectrum of the induction-spark from the metal is examined. This is most clearly seen in the case of the calcium spectrum. I have found that if a wet string, or a narrow tube filled with water, be placed in the metallic circuit joining the Leyden jar which gives the spark, and if the electrodes be moistened with a solution of chloride of calcium, a spectrum is obtained which coincides precisely with that seen when a chloride of calcium band is placed in the colourless gas-flame. Those lines appear absent which are the most distinct when an extra metallic circuit is employed. If the narrow column of water be replaced by a column of larger sectional area and of a shorter length, a spectrum is produced in which both those lines seen in the flame, and those obtained by the intense spark, are equally plainly visible. In this experiment we see the mode in which the calcium spectrum, as given in the flame, changes into that produced by the bright electric spark."—Kirchhoff on the "Researches of the Solar Spectrum and the Spectra of the Chemical Elements," translated by Dr. Roscoe.

coincident. And as regards salts of the other metals, M. Alexander Mitscherlich states that he has found that the chlorides and iodides of copper give distinct spectra, according to the order of combination to which they belong, and that sulphide of copper gives no spectrum.*

1549. *Do any of the lines of different metals coincide?*— It is as yet impossible to decide, owing to the infancy of the discovery, whether all the lines of the different metals occupy distinct positions in the spectrum if sufficiently dispersed, or whether some of them are not coincident; it was at one time supposed that a line in the lithium spectrum was coincident with a line in the strontium spectrum, but Professors Roscoe and Clifton, when they examined it with a spectroscope of three prisms, found that they were not coincident, but that there was an interval between them, the lithium line being the most refrangible. It was also believed that a green line in the spectrum of thallium was coincident with one of the lines in the spectrum of baryta; but M. Gassiott has ascertained, with a spectroscope of nine prisms, that they do not coincide; the thallium line is clearly seen, by the aid of this instrument, to occupy a dark space in the baryta spectrum close by the bright line with which it was supposed to coincide. "If we compare," states Kirchhoff,* "the spectra of the different metals with each other, several of the bright lines appear to coincide. This is especially noticeable in the case of an iron and magnesium line, and with an iron and calcium line. It seems to me," he says, "to be a question of great interest to determine whether these and other similar coincidences are real or only apparent; whether the lines in question actually fall one upon the other, or whether they lie very close together. I believe that my method of observation does not possess the requisite accuracy for the purpose of answering this question with any degree of probability, and I think that a larger number of prisms and an increased intensity of the light will prove necessary. This might, probably, be accomplished by substituting the continuous current of a powerful battery for the induction spark of a Ruhmkorff's coil."

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* "At the close of this Memoir we cannot refrain from touching upon a question to which, on some future occasion, we must again recur. Amongst the large number of those salts already examined by us, which, owing to their volatility in the flame, render a spectrum analysis possible, we have not found, in spite of the great variation in the elementary bodies combined with the metal, a single one which failed to produce the characteristic bright lines of the metal. Considering these numerous observations, made under the most widely differing circumstances, we might be led to suppose that in *all cases* the bright lines given out by a body occur quite independently of the other elements chemically combined with that body, and that therefore the relation of the elements, as regards the spectra of their vapours, is exactly the same, whether they are free or chemically combined. Yet this supposition is by no means founded on fact We have repeatedly insisted that the bright lines in the spectrum of a luminous gas must coincide with the absorption lines which this gas produces in a continuous spectrum of a sufficient degree of luminosity. It is well known that the absorption lines of iodine vapour cannot be produced by hydriodic acid, and that, on the other hand, the absorption lines of nitrous acid are not visible in a mechanical mixture of nitrogen and oxygen. There is nothing to show why an influence of chemical combination upon the absorption lines, similar to that here noticed at low temperatures, should not occur at a white heat. If, however, the state of chemical combination alters the absorption lines of a luminous gas, it *must* likewise alter the bright lines of its spectrum.

"From these considerations one would conclude that in the case of the spectra of two different compounds of the same metal, different bright lines may appear; it is, however, possible that the salts which are volatilized in the flame cannot exist at the temperature of the flame, and are decomposed, so that it may be in reality the vapour of the free metal which produces the lines; and it would then appear quite possible that a chemical compound may produce bright lines differing from those produced by its constituent elements."—"On Chemical Analysis by Spectrum." Observations by Professors Bunsen and Kirchhoff. *Phil. Mag.*, 1861.

1550. *Are the lines of any substance obliterated or altered by the presence of another substance?* — There arises another question, which is closely connected with the subject of the last paragraph; it is this:—Are the lines of any substance obliterated or altered by the presence of any other substance? M. A. Mitscherlich has lately communicated the results of some experiments which he has made on this subject; he states that the spectrum given by chloride of barium in presence of excess of hydrochloric acid is quite different to the spectrum of barium itself. He also noticed that the spectra of the chlorides of calcium and strontium, in presence of hydrochloric acid, are different to the spectra of calcium and strontium; and that a solution of chloride of potassium, in presence of chloride of ammonium and excess of hydrochloric acid, gives no spectrum, whilst a solution of chloride of potassium by itself, and when much more diluted, gives the characteristic lines of potassium. He also states that the blue rays of chloride of strontium disappear in the presence of the spectrum produced by chloride of copper with addition of chloride of ammonium.

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* "Researches on the Solar Spectrum and the Spectra of the Chemical Elements."

1551. *Spectra of the metalloids.*—The incandescent vapours of the metalloids, as well as the vapours of the metals, give spectra; and, as in the case of the metals, each metalloid gives a spectrum peculiar to itself: carbon, for instance, gives a spectrum consisting of several blue lines; hydrogen gives off only two kinds of light, a bright red line and a bright blue line; nitrogen gives beautiful violet lines. Some of the elements, so far as it is yet ascertained, do not give peculiar lines; arsenic, antimony, and sulphur, for instance, give continuous spectra, but perhaps, under other conditions, they will give distinct spectra.

1552. *The spectra of solids and vapours contrasted.*—We must now direct the student's attention to the difference in the spectra of solid bodies at a white heat and the spectra of incandescent bodies in a state of vapour. Solid bodies, when *white hot*, emit light of all degrees of refrangibility, each particular refrangibility corresponding to a particular colour, whilst we have seen that incandescent vapours and gases emit light of only certain degrees of refrangibility; the spectra of solids at a white heat are therefore continuous,* that is, there is no gap or interval between the colours, whilst the spectra of incandescent vapours and gases are not continuous, because there are lines of light of different degrees of refrangibility absent, consequently the spaces these lines would fill in the spectra, if present, are unoccupied; these blank spaces, therefore, appear as black bands or lines, and they indicate the absence from the spectra of certain lines of light, and the position these lines would occupy if they were present. In order to carry out the contrast still further between the spectra of solids and vapours, we must consider the different effects produced upon solids at different temperatures. The fact is universally known that solids may be heated to a certain extent without becoming luminous; at that temperature they give off dark or non-luminous rays of heat; if they are heated beyond this they will become luminous, but until they reach a white heat they only give off certain rays of light, these varying with the temperature. At the lowest visible stage of temperature solids give off red rays; they are then said to be red hot: at a still higher temperature they give off yellow rays; they are then said to be yellow hot: at a still higher temperature they give off blue rays; they are then said to be bluish hot: and at a still higher temperature they give off rays of every degree of refrangibility,—they then produce on the eye the sensation of whiteness, and are said to be white hot. Now all solid bodies, when heated, emit the same rays of light, but each incandescent vapour emits rays peculiar to itself, no other vapour emitting rays of the same degree of refrangibility. The rays of light emitted by vaporous bodies, or at least by some, increase with increase of temperature, and some which are seen at a lower temperature become invisible and are replaced by others at a high temperature, but it appears unlikely that there should be a degree of temperature with vapours, as with solids, at which they would emit rays of all degrees of refrangibility, although it is worth observing that one of the most volatile of the metals, potassium, gives a partially continuous spectrum, and such volatile bodies as arsenic, antimony, and sulphur, give only continuous or confused spectra, so far as yet known.

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* Liquids also give continuous spectra.

1553. *Relation between the absorption and emission of heat and light by bodies.*—Mr. Balfour Stewart, in 1858, discovered a law with regard to the relation between the absorption and emission of heat by bodies, which has been called the law of exchanges; it may be thus expressed,—that the relation between the amount of heat emitted and that which is absorbed, at *any given temperature*, remains *constant for all bodies*, and that the greater the amount of heat emitted, the greater must be the amount of heat absorbed. Kirchhoff has shown that the same law holds good of luminous as of heat-giving rays. The conclusion at which he has arrived may be thus stated,—that when any substance is heated, or is rendered luminous, rays of a certain degree of refrangibility are given out by it, whilst the same substance has also the power of absorbing rays of this identical refrangibility, so that every substance which emits, at a *given temperature*, certain kinds of light, possesses the power, at the same temperature, of absorbing the same kind of light. The following experiment is an illustration of this law:—The spectrum of the oxy-hydrogen lime light, like the spectrum of all other solid and liquid bodies, is continuous; it contains no dark lines: if, however, the light from the intensely heated lime be made to pass through a flame coloured yellow with a sodium compound, it will be found there are now dark lines in its spectrum, corresponding in position to the sodium lines. This fact is easily explained in accordance with the law which has just been enunciated; the sodium flame has absorbed that kind of light which it emits, whilst it is perfectly transparent for all other rays; hence all the rays of light from the lime appear in the spectrum when it is passed through a flame coloured with sodium, excepting those rays which are of the same degree of refrangibility as those emitted by incandescent sodium compounds;* it is just as easy to reverse the red lithium line, that is, to turn the bright line emitted by lithium into a dark one, by allowing the lime light to traverse a flame coloured with lithium, as it is to reverse the sodium line. It is not so easy to obtain the reversal of the spectra of the other metals; nevertheless, Bunsen and Kirchhoff have succeeded in reversing the bright lines of potassium, strontium, calcium, and barium, and Dr. Miller has reversed some of the strongest lines in the spectrum of copper.†

1554. *Dark lines in the solar spectrum.*—"The colours of the solar spectrum are not continuous, but are interspersed with numerous dark spaces, which, in some cases, indicate the line of demarcation between two adjacent colours. Some of these spaces are composed of a series of fine lines grouped together, while others consist of thick dark stripes. When the spectrum is not very well defined, these lines appear as shadows. They were first discovered by Wollaston; but as Frauenhofer was the first to study them in a complete manner, they are called *Frauenhofer's lines*.

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* "The absorptive power of sodium vapour becomes most apparent when its luminosity is smallest, or when its temperature is lowest. In fact, we (Bunsen and Kirchhoff) were unable to produce the dark sodium lines in the spectrum of the lime light, or in that of an incandescent platinum wire, by means of a Bunsen's gas-flame in which common salt was placed, but the experiment succeeded with a flame of aqueous alcohol containing common salt."—"Researches on the Solar Spectrum," by Professor Kirchhoff.

† "If the source of light giving a continuous spectrum, by means of which the spectrum of a glowing gas is to be reversed, be an incandescent body, its temperature must be higher than that of the glowing gas."—*Ibid.*

1555. "They are best observed by allowing a pencil of solar rays, reflected from a heliostat, to pass into a dark chamber through a narrow slit. The pencil is received, at a distance of three or four yards, on a flint glass prism, or on a hollow prism filled with some powerfully dispersive liquid. When a telescope is held behind the prism, in the direction of the refracted ray, a very distinct spectrum is seen, with the dark lines. The greater the magnifying power, the greater the number of lines. Frauenhofer observed six hundred, and Wollaston several thousands. In the solar spectrum the succession of these lines is always the same, whatever be the nature of the prism and whatever its angle. There are seven sets of lines which are more distinct than the rest, and are especially known as *Frauenhofer's lines*.

1556. *The dark lines vary with the nature of the luminous source.*—"The dark lines vary with the nature of the luminous source. The light reflected from the sun—that is, the light from the planets—produces the same dark lines as the sun, but the spectra of the fixed stars are different. That of Sirius contains three remarkable lines, one in the green and two in the blue."*

1557. *The solar spectrum and the spectrum of an incandescent solid or liquid contrasted.*—The spectrum furnished by an incandescent solid or liquid differs then from the solar spectrum, inasmuch as the first yields a continuous band of light, whilst the latter does not, as black bands or lines (Frauenhofer's lines) intersect the differently coloured portions of its spectrum: these dark lines have been a puzzle to philosophers. Although Frauenhofer observed, as early as the year 1814, that the two dark lines in the solar spectrum, which he named D, coincided with the yellow lines, which we know, but he did not, to be the sodium lines; and although Sir David Brewster, in the year 1842, observed that a line in the potassium spectrum coincided with the dark solar line named A, the connection between the dark solar lines and the bright lines of the elementary bodies was unknown, although not quite unsuspected, until Kirchhoff in 1859 revealed the secret, and placed it, at the same time, in our power to examine the chemical constitution of the sun and the fixed stars.

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* Ganot's "Physics," edited by Dr. Atkinson.

1558. *Chemical constitution of the sun's atmosphere.*—Kirchhoff has found that the bright lines produced by the incandescent vapours of iron, nickel, chromium, calcium, magnesium, potassium, sodium, barium, zinc, and copper, coincide with dark solar lines; and the coincidence is rendered still more remarkable when we take into consideration the number of bright lines each of these metals yields, and that each bright line of the metal coincides with a dark solar line; iron, for instance, yields not less than sixty bright lines, and they coincide with as many dark solar lines, and not only do they coincide, but, as a rule, the brighter the metallic line the darker the solar line. Hence, as Kirchhoff observes, this coincidence must be produced by some cause, and a cause, he states, can be assigned which affords a perfect explanation. If we suppose the sun is a solid or liquid nucleus intensely heated, —and it is the most probable supposition we can make respecting the sun's constitution,—it will give, like all other incandescent solids or liquids, a continuous spectrum. We have seen that a continuous spectrum can be rendered discontinuous or broken, if the light traverse an atmosphere of some vaporized substance, less intensely heated than the incandescent solid or liquid which is yielding the continuous spectrum, for the vaporized substance absorbs light of the same refrangibility which it emits; in other words, it absorbs that kind of light which it emits, whilst it allows all other kinds of light to pass through it. The spectrum of the sun, like the spectrum of any other incandescent solid or liquid, would be rendered discontinuous or broken, if the light traversed an atmosphere containing any vaporized substance; therefore, if the light of the sun were to traverse an atmosphere of a somewhat lower temperature, containing iron, nickel, chromium, calcium, magnesium, potassium, sodium, barium, zinc, and copper vapours, according to the law of exchanges, there would be dark lines in the solar spectrum in place of the bright lines which these metals yield, for these vaporized metals would remove from the continuous spectrum of the sun those colours which they themselves emit, consequently there would be dark lines in the solar spectrum which would coincide with the bright metallic lines emitted by these metals in a vaporized state. Kirchhoff has found that there are dark lines in the solar spectrum which coincide with the bright lines of the metals we have named, and therefore he concludes that rays of light which form the solar spectrum have passed through the vapours of these metals, and have thus suffered the absorption which these metallic vapours must exert. "These metallic vapours might be contained either in the atmosphere of the sun or in that of the earth. But it is not easy to understand how our atmosphere can contain such a quantity of metallic vapours as would produce the very distinct absorption-lines which we see in the solar spectrum; and this supposition is rendered still less probable by the fact that these lines do not appreciably alter when the sun approaches the horizon. It does not, on the other hand, seem at all unlikely, owing to the high temperature which we must suppose the sun's atmosphere to possess, that such vapours should be present in it. Hence the observations of the solar spectrum appear to me to prove the presence of metallic vapours in the solar atmosphere with as great a degree of certainty as we can obtain in any question of natural science." Barium, copper, and zinc appear to be present only in small quantities in the solar atmosphere, as the brightest of the lines of those metals correspond to distinct lines in the solar spectrum, but the weaker lines are not noticeable. Some of the cobalt lines, but not all, coincide with dark solar lines; it is therefore uncertain whether this metal is present in the solar atmosphere. The remaining metals which Kirchhoff has examined, viz., gold, silver, mercury, aluminum, cadmium, tin, lead, antimony, arsenic, strontium, and lithium, are, according to his observations, not visible in the solar atmosphere.

1559. *Chemical constitution of the atmosphere of the fixed stars.*—As there are dark lines in the spectra of the fixed stars which are not in the solar spectrum, their atmosphere must contain substances which are not present in that of the sun.

APPENDIX N.

1560. *Arrangement of the spectrum apparatus.*[*]—The telescope, F, is first drawn out so far that a distant object is plainly seen, and screwed into the ring in which it is held, care being taken to loosen the screws *g* and *h* beforehand. The tube, D, is then brought into its place, and the axis of F brought into one straight line with that of D. The slit is then drawn out until it is distinctly seen on looking through the telescope, and this latter is then fixed by moving the screws *g* and *h*, so that the middle of the slit is seen in about the middle of the field of view. After removing the small spring, *c*, the prism is next placed on the brass plate, and fastened in the position which is marked first, and secured by screwing down the spring, *c*. If the axis of the tube, D, be now directed towards a bright surface, such as the flame of a candle, the spectrum of the flame is seen in the lower half of the field of the telescope on moving the latter through a certain angle round the axis of the foot, A. When the telescope has been placed in position, the tube, I, is fastened on to the arm belonging to it, and this is turned through an angle round the axis of the foot such that, when a light is allowed to fall on the divided scale, the image of the scale is seen through the telescope, F, reflected from the nearer face of the prism. This image is brought exactly into focus by altering the position of the scale in tube I; and by turning this tube on its axis, it is easy to make the line, in which one side of the divisions on the scale lie, parallel with the line dividing the two spectra, and by means of the screw connected with I to bring these two lines to coincide.

In order to bring the two sources of light, K and L, into position, two methods may be employed. One of these depends upon the existence of bright lines in the inner cone of the colourless gas-flame. If the lamp, L, be pushed past the slit, a point is easily found at which these lines become visible. The lamp must then be pushed still further to the left, until these lines nearly or entirely disappear. The right mantle of the flame is now before the slit, and into this the bead of substance under examination must be brought. In the same way the position of the source of light, K, may be ascertained.

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[*] Bunsen and Kirchhoff on "Spectrum Analysis." *Phil. Mag.*, 1861.

The second method is as follows:—The telescope, F, is so placed that the brightest portion of the spectrum of the flame of a candle is seen in about the middle of the field of view. The flame is then placed before the ocular in the direction of the axis of the telescope, and the position before the slit determined, in which the upper half of the slit appears to be brightest. The lamp, L, is then placed so that the slit appears behind that portion of the flame from which the most light is given off, after the introduction of the bead. In a similar way, the position of the lamp, K, is determined by looking through the small prism and the lower half of the slit.

By means of the screw, *e*, the breadth of the slit can be regulated in accordance with the intensity of the light, and the degree of purity of the spectrum which is required. The illumination of the scale is best effected by means of a luminous gas flame placed before it. The light can, if necessary, be lessened by placing a silver paper screen close before the scale. The degree of illumination suited to the spectrum under examination can then be easily found by placing this flame at different distances.

APPENDIX.—I.

Weights and measures, page 717. *Table I.—Specific gravity and absolute weight of several gases, page* 720. *Table II.—Weight of one cubic centimetre of air at different temperatures, page* 721. *Table III.—For the conversion of degrees on the Centigrade scale into Fahrenheit degrees, page* 723.

Weights and measures.—The following tables of English weights and measures are those used in science and commerce. In these the student will find the subdivisions of the two English pounds, with their equivalents in French grammes on the metrical system.

"The two systems of weights, called *troy* and *avoirdupois*, have no common integer except the *grain*. Although the names, pound, ounce, and drachm, are common to both systems, they denote different quantities in each. The English *troy* pound is subdivided into 12 ounces, and each ounce is equal to 480 grains. The subdivisions of the troy ounce, called *apothecaries' weight*, are into 8 drachms, each drachm into 3 scruples, and each scruple into 20 grains. The troy ounce is also divided into 20 pennyweights, of 24 grains each. These are the weights generally employed; but for philosophical purposes ambiguity is most easily avoided by employing the *grain* as integer, and the laboratory should be provided with good sets of weights, from 1,000 grains downwards: the grain should be decimally subdivided into tenths, hundredths, and thousandths."

Apothecaries' Weight.

Pound.		Ounces.		Drachms.		Scruples.		Grains.		Fr. grms.
1	=	12	=	96	=	288	=	5760	=	372·96
		1	=	8	=	24	=	480	=	31·08
				1	=	3	=	60	=	3·885
						1	=	20	=	1·295
								1	=	0·0647

Avoirdupois Weight.

Pound.		Ounces.		Drachms.		Grains.		Fr. grms.
1	=	16	=	256	=	7000	=	453·25
		1	=	16	=	437·5	=	28·328
				1	=	27·343	=	1·77

Measures of volume.—"Weights are connected with measures by the subdivisions of the imperial gallon. The weight of an imperial gallon of absolutely pure water, at 30 inches pressure and 62°, is *ten avoirdupois pounds*, or 70,000 grains. It is equal to 277·274 cubic inches. It is one-fifth more than the old wine gallon, *i. e.*, 30 imperial are = 36 wine gallons."

IMPERIAL MEASURE.

Gallon.		Pints.		Fluid ounces.		Fluid drachms.		Minims.
1	=	8	=	160	=	1,280	=	76,800
		1	=	20	=	160	=	9,600
				1	=	8	=	480
						1	=	60

WEIGHT OF WATER AT 62°.

Measure.		Cubic inches.		Grains.
1 gallon	=	277·274	=	70,000
1 quart	=	69·318	=	17,500
1 pint	=	34·659	=	8,750
16 fluid ounces	=	27·727	=	7,000
1 fluid ounce	=	1·732	=	437·5
1 fluid drachm	=	0·216	=	54·7
1 minim	=	0·0336	=	0·91

The weight of *one cubic inch* of distilled water at 62° is 252·458 grains. The troy ounce of distilled water, which contains 480 grains, is equal to 1·8047 cubic inches. The wine pint corresponds to 28·875, and the imperial pint to 34·65 cubic inches at 60°."

THE METRICAL SYSTEM.—"The French metre is equal to 39·370788 English inches. The *metre* is, in France, the integer of the measure of *length*, and from it all measures of surface, capacity, and weight are derived. The integer of the measure of capacity is the *litre*, which is the cubed decimetre, and is equal to 35·275 fluid ounces, or 1·763 imperial pints. The integer of the measure of weight is the *gramme*, = 15·434 English grains. It is exactly equal to the weight of a *cubic centimetre* of water, weighed *in vacuo* at its maximum density (39°·38). The cubic centimetre is employed by French chemists in all measurements of gases, in place of our cubic inch. It is equal to 0·061 of a cubic inch. The weight of the cubic centimetre of water is to the cubic inch of water as 15·434 to 252·458; hence there are 16·34 cubic centimetres to an English cubic inch.

"This rule is sufficiently correct for practical purposes. It is to be observed, however, that the French take the weight of the cubic centimetre of water at 39·38 *in vacuo*. The English take the weight of the cubic inch (252·458 grains) at 62° in air. Assuming the specific gravity of water at 32° to be 1·000000, the specific gravity at 39·38 is to the specific gravity at 62° as 1·000099 to 0·999000.

"The French measures increase and decrease in decimal proportions. For the *increase*, a prefix is used derived from the Greek *deca*, *hecto*, *kilo*, and *myria;* the integer, whether metre, litre, or gramme, being multiplied by 10, 100, 1,000, and 10,000 respectively. To indicate the *decrease*, the prefixes *deci*, *centi*, and *milli*, derived from the Latin, are employed. In this case the integer is supposed to be divided by 10, 100, or 1,000.

"Various plans have been devised for converting the French weights and measures into their English equivalents. The following tables will be found useful for this purpose:—

Measures of Length.

		English inches.
Millimètre	=	·03937
Centimètre	=	·39371
Decimètre	=	3·93708
Mètre	=	39·37079
Decamètre	=	393·70788
Hectomètre	=	3,937·0788
Kilomètre	=	39,370·788
Myriamètre	=	393,707·88

Measures of Volume.

		Cubic inches.
Millilitre	=	·06103
Centilitre	=	·61028
Decilitre	=	6·1028
Litre	=	61·028
Decalitre	=	610·28
Hectolitre	=	6,102·8
Kilolitre	=	61,028
Myrialitre	=	610,280

Measures of Weight.

		English grains.
Milligramme	=	·0154
Centigramme	=	·1543
Decigramme	=	1·5434
Gramme	=	15·434
Decagramme	=	154·34
Hectogramme	=	1,543·4
Kilogramme	=	15,434
Myriagramme	=	154,340

"A kilogramme is equal to 2·2046 pounds avoirdupois; and 1,000 kilogrammes are equal to an English ton. The quintal, or 50 kilogrammes, is equal to the English cwt. With respect to the equivalents of English and French weights and measures, some slight differences will be found among English writers. These arise from the calculations being based on the employment of a larger or smaller number of decimal figures."

SURFACES AND CAPACITIES.—"*Surface of a sphere*=diameter squared × 3·141593. *Capacity of a sphere*=diameter cubed × 0·5236. *Area of a circle*=diameter squared × 0·785938. *Area of rectangle, square rhombus, and rhomboid*=base × by height. *Capacity of the prism or cylinder* (rule for calculating the capacities of cylindrical vessels used for gases)=area of the base × by height."*

TABLE I.—*Specific gravity and absolute weight of several gases.*

	Specific grav. Atmospheric air = 1·000.	1 litre (1,000 cubic centimetres) of gas at 0° C. and 0·76 metre bar pressure weighs grammes.
Atmospheric air - -	1·000	1·29363
Oxygen - - -	1·10563	1·43028
Hydrogen - - -	0·06910	0·08939
Water, vapour of - -	0·62192	0·80453
Carbon, vapour of -	0·82922	1·07270
Carbonic acid - -	1·52024	1·96663
Carbonic oxide - -	0·96743	1·25150
Phosphorus, vapour of -	4·33452	5·60727
Sulphur, vapour of -	6·63378	8·58165
Hydrosulphuric acid -	1·17475	1·51969
Iodine, vapour of - -	8·76760	11·34203
Bromine, vapour of -	5·52605	7·14866
Chlorine - - -	2·45052	3·17007
Nitrogen - - -	0·96776	1·25192
Ammonia - - -	0·58753	0·76005

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* Brande and Taylor's "Manual of Chemistry."

TABLE II.—*Weight of one cubic centimetre of atmospheric air at different temperatures, from 0° to 300° C. (grammes).*

0°	0·001293	39°	0·001131	78°	0·001005	117°	0·000905
1	0·001288	40	0·001128	79	0·001002	118	0·000903
2	0·001284	41	0·001124	80	0·001000	119	0·000900
3	0·001279	42	0·001121	81	0·000997	120	0·000898
4	0·001275	43	0·001118	82	0·000994	121	0·000896
5	0·001270	44	0·001114	83	0·000992	122	0·000894
6	0·001266	45	0·001111	84	0·000989	123	0·000891
7	0·001261	46	0·001108	85	0·000986	124	0·000889
8	0·001257	47	0·001105	86	0·000983	125	0·000887
9	0·001252	48	0·001102	87	0·000980	126	0·000884
10	0·001248	49	0·001098	88	0·000977	127	0·000882
11	0·001243	50	0·001095	89	0·000974	128	0·000880
12	0·001239	51	0·001091	90	0·000972	129	0·000878
13	0·001234	52	0·001088	91	0·000969	130	0·000876
14	0·001230	53	0·001084	92	0·000967	131	0·000874
15	0·001225	54	0·001081	93	0·000964	132	0·000871
16	0·001221	55	0·001077	94	0·000962	133	0·000869
17	0·001217	56	0·001074	95	0·000959	134	0·000867
18	0·001213	57	0·001070	96	0·000956	135	0·000865
19	0·001209	58	0·001067	97	0·000953	136	0·000863
20	0·001205	59	0·001063	98	0·000951	137	0·000860
21	0·001201	60	0·001060	99	0·000948	138	0·000858
22	0·001197	61	0·001057	100	0·000946	139	0·000856
23	0·001193	62	0·001053	101	0·000943	140	0·000854
24	0·001189	63	0·001050	102	0·000941	141	0·000852
25	0·001185	64	0·001047	103	0·000938	142	0·000850
26	0·001181	65	0·001044	104	0·000936	143	0·000848
27	0·001177	66	0·001041	105	0·000933	144	0·000846
28	0·001173	67	0·001038	106	0·000931	145	0·000844
29	0·001169	68	0·001035	107	0·000928	146	0·000842
30	0·001165	69	0·001032	108	0·000926	147	0·000840
31	0·001161	70	0·001029	109	0·000923	148	0·000838
32	0·001157	71	0·001026	110	0·000921	149	0·000836
33	0·001154	72	0·001023	111	0·000919	150	0·000834
34	0·001150	73	0·001020	112	0·000916	151	0·000832
35	0·001146	74	0·001017	113	0·000914	152	0·000830
36	0·001142	75	0·001014	114	0·000911	153	0·000828
37	0·001138	76	0·001011	115	0·000909	154	0·000826
38	0·001134	77	0·001008	116	0·000907	155	0·000824

TABLE II.—*continued.*

156°	0·000822	193°	0·000757	229°	0·000702	265°	0·000655
157	0·000821	194	0·000755	230	0·000701	266	0·000654
158	0·000819	195	0·000754	231	0·000699	267	0·000653
159	0·000817	196	0·000752	232	0·000698	268	0·000652
160	0·000815	197	0·000751	233	0·000697	269	0·000651
161	0·000813	198	0·000749	234	0·000695	270	0·000650
162	0·000811	199	0·000748	235	0·000694	271	0·000648
163	0·000809	200	0·000746	236	0·000692	272	0·000647
164	0·000807	201	0·000744	237	0·000691	273	0·000646
165	0·000806	202	0·000743	238	0·000690	274	0·000645
166	0·000804	203	0·000740	239	0·000689	275	0·000643
167	0·000802	204	0·000739	240	0·000688	276	0·000642
168	0·000800	205	0·000737	241	0·000686	277	0·000641
169	0·000798	206	0·000736	242	0·000685	278	0·000640
170	0·000796	207	0·000734	243	0·000683	279	0·000639
171	0·000794	208	0·000733	244	0·000682	280	0·000638
172	0·000793	209	0·000731	245	0·000681	281	0·000636
173	0·000791	210	0·000730	246	0·000679	282	0·000635
174	0·000789	211	0·000728	247	0·000678	283	0·000634
175	0·000788	212	0·000727	248	0·000677	284	0·000633
176	0·000786	213	0·000725	249	0·000675	285	0·000631
177	0·000784	214	0·000724	250	0·000674	286	0·000630
178	0·000782	215	0·000722	251	0·000673	287	0·000629
179	0·000781	216	0·000721	252	0·000672	288	0·000628
180	0·000779	217	0·000719	253	0·000670	289	0·000627
181	0·000777	218	0·000718	254	0·000669	290	0·000626
182	0·000776	219	0·000716	255	0·000668	291	0·000625
183	0·000774	220	0·000715	256	0·000666	292	0·000624
184	0·000772	221	0·000713	257	0·000665	293	0·000623
185	0·000770	222	0·000712	258	0·000664	294	0·000622
186	0·000769	223	0·000710	259	0·000663	295	0·000621
187	0·000767	224	0·000709	260	0·000662	296	0·000620
188	0·000765	225	0·000708	261	0·000660	297	0·000619
189	0·000763	226	0·000706	262	0·000659	298	0·000618
190	0·000762	227	0·000705	263	0·000658	299	0·000617
191	0·000760	228	0·000703	264	0·000657	300	0·000616
192	0·000758						

TABLE III.—*For the conversion of degrees on the Centigrade thermometer into degrees of Fahrenheit's scale.*

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
— 40°	— 40·0	— 1°	+ 30·2	+ 38°	+ 100·4	+ 77°	+ 170·6
39	38·2	0	32·0	39	102·2	78	172·4
38	36·4	+ 1	33·8	40	104·0	79	174·2
37	34·6	2	35·6	41	105·8	80	176·0
36	32·8	3	37·4	42	107·6	81	177·8
35	30·0	4	39·2	43	109·4	82	179·6
34	29·2	5	41·0	44	111·2	83	181·4
33	27·4	6	42·8	45	113·0	84	183·2
32	25·6	7	44·6	46	114·8	85	185·0
31	23·8	8	46·4	47	116·6	86	186·8
30	22·0	9	48·2	48	118·4	87	188·6
29	20·2	10	50·0	49	120·2	88	190·4
28	18·4	11	51·8	50	122·0	89	192·2
27	16·6	12	53·6	51	123·8	90	194·0
26	14·8	13	55·4	52	125·6	91	195·8
25	13·0	14	57·2	53	127·4	92	197·6
24	11·2	15	59·0	54	129·2	93	199·4
23	9·4	16	60·8	55	131·0	94	201·2
22	7·6	17	62·6	56	132·8	95	203·0
21	5·8	18	64·4	57	134·6	96	204·8
20	4·0	19	66·2	58	136·4	97	206·6
19	2·2	20	68·0	59	138·2	98	208·4
18	0·4	21	69·8	60	140·0	99	210·2
17	+ 1·4	22	71·6	61	141·8	100	212·0
16	3·2	23	73·4	62	143·6	101	213·8
15	5·0	24	75·2	63	145·4	102	215·6
14	6·8	25	77·0	64	147·2	103	217·4
13	8·6	26	78·8	65	149·0	104	219·2
12	10·4	27	80·6	66	150·8	105	221·0
11	12·2	28	82·4	67	152·6	106	222·8
10	14·0	29	84·2	68	154·4	107	224·6
9	15·8	30	86·0	69	156·2	108	226·4
8	17·6	31	87·8	70	158·0	109	228·2
7	19·4	32	89·6	71	159·8	110	230·0
6	21·2	33	91·4	72	161·6	111	231·8
5	23·0	34	93·2	73	163·4	112	233·6
4	24·8	35	95·0	74	165·2	113	235·4
3	26·6	36	96·8	75	167·0	114	237·2
2	28·4	37	98·6	76	168·8	115	239·0

Table III.—*continued.*

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
+116°	+240·8	+156°	+312·8	+196°	+384·8	+236°	+456·8
117	242·6	157	314·6	197	386·6	237	458·6
118	244·4	158	316·4	198	388·4	238	460·4
119	246·2	159	318·2	199	390·2	239	462·2
120	248·0	160	320·0	200	392·0	240	464·0
121	249·8	161	321·8	201	393·8	241	465·8
122	251·6	162	323·6	202	395·6	242	467·6
123	253·4	163	325·4	203	397·4	243	469·4
124	255·2	164	327·2	204	399·2	244	471·2
125	257·0	165	329·0	205	401·0	245	473·0
126	258·8	166	330·8	206	402·8	246	474·8
127	260·6	167	332·6	207	404·6	247	476·6
128	262·4	168	334·4	208	406·4	248	478·4
129	264·2	169	336·2	209	408·2	249	480·2
130	266·0	170	338·0	210	410·0	250	482·0
131	267·8	171	339·8	211	411·8	251	483·8
132	269·6	172	341·6	212	413·6	252	485·6
133	271·4	173	343·4	213	415·4	253	487·4
134	273·2	174	345·2	214	417·2	254	489·2
135	275·0	175	347·0	215	419·0	255	491·0
136	276·8	176	348·8	216	420·8	256	492·8
137	278·6	177	350·6	217	422·6	257	494·6
138	280·4	178	352·4	218	424·4	258	496·4
139	282·2	179	354·2	219	426·2	259	498·2
140	284·0	180	356·0	220	428·0	260	500·0
141	285·8	181	357·8	221	429·8	261	501·8
142	287·6	182	359·6	222	431·6	262	503·6
143	289·4	183	361·4	223	433·4	263	505·4
144	291·2	184	363·2	224	435·2	264	507·2
145	293·0	185	365·0	225	437·0	265	509·0
146	294·8	186	366·8	226	438·8	266	510·8
147	296·6	187	368·6	227	440·6	267	512·6
148	298·4	188	370·4	228	442·4	268	514·4
149	300·2	189	372·2	229	444·2	269	516·2
150	302·0	190	374·0	230	446·0	270	518·0
151	303·8	191	375·8	231	447·8	271	519·8
152	305·6	192	377·6	232	449·6	272	521·6
153	307·4	193	379·4	233	451·4	273	523·4
154	309·2	194	381·2	234	453·2	274	525·2
155	311·0	195	383·0	235	455·0	275	527·0

Table III.—*continued.*

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
+276°	+528·8	+298°	+568·4	+319°	+606·2	+340°	+644·0
277	530·6	299	570·2	320	608·0	341	645·8
278	532·4	300	572·0	321	609·8	342	647·6
279	534·2	301	573·8	322	611·6	343	649·4
280	536·0	302	575·6	323	613·4	344	651·2
281	537·8	303	577·4	324	615·2	345	653·0
282	539·6	304	579·2	325	617·0	346	654·8
283	541·4	305	581·0	326	618·8	347	656·6
284	543·2	306	582·8	327	620·6	348	658·4
285	545·0	307	584·6	328	622·4	349	660·2
286	546·8	308	586·4	329	624·2	350	662·0
287	548·6	309	588·2	330	626·0	351	663·8
288	550·4	310	590·0	331	627·8	352	665·6
289	552·2	311	591·8	332	629·6	353	667·4
290	554·0	312	593·6	333	631·4	354	669·2
291	555·8	313	595·4	334	633·2	355	671·0
292	557·6	314	597·2	335	635·0	356	672·8
293	559·4	315	599·0	336	636·8	357	674·6
294	561·2	316	600·8	337	638·6	358	676·4
295	563·0	317	602·6	338	640·4	359	678·2
296	564·8	318	604·4	339	642·2	360	680·0
297	566·6						

APPENDIX II.

In this Appendix is given a selection of questions from the last two years' examination papers on chemistry of the MUSEUM OF IRISH INDUSTRY, the ROYAL SCHOOL OF MINES, the LONDON UNIVERSITY, TRINITY COLLEGE, DUBLIN, the QUEEN'S COLLEGES of BELFAST and CORK, the QUEEN'S UNIVERSITY of IRELAND, the EXAMINATION for SCIENCE CERTIFICATES and SCIENCE SCHOOLS DEPARTMENT of SCIENCE and ART, which can be answered either from this book or my other two works, viz., the "First Step in Chemistry," and the "Qualitative Analysis."

I have employed the following contractions:—S. S. for "Second Step in Chemistry," F. S. for "First Step," and Q. A. for "Qualitative Analysis;" par. for paragraph.

MUSEUM OF IRISH INDUSTRY.*

1862.

Write the formulæ, and state briefly the more important physical and chemical properties, of the compounds of hydrogen with S, Cl, N, Te, P, Br, As, Fl, Se, Sb, I; and give in each case the volumes of the constituents before combination, and the volume of the compound, compared with the volume of the equivalent of oxygen = 1.—[S. S., pars. 269 to 271.]

Write the formulæ of the following glycerides:—Monostearine, dichlorhydrine, tributyrine. What would be the action of potash upon them? and apply the reaction to explain the process of saponification.—[S. S., pars. 834 to 869.]

Define what acids, bases, and salts are, according—1, to the acid and base theory; and, 2, the salt radical theory;

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* The old atomic weights of carbon = 6, and oxygen = 8, are to be adopted in answering the Museum questions. Water is therefore represented by formula $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$.

and illustrate your explanation by showing, by means of symbols, the action of a hydrogen acid, and of a hydrated acid upon a base.—[S. S., pars. 219 to 230.]

Show by means of symbols how the following bodies may be supposed to be derived from water, with the equivalent doubled $H_2 O_2$:—Hydrated potash, anhydrous potash, monohydrated nitric acid, anhydrous nitric acid, carbonate of potash, amylic alcohol ($C_{10} H_{12} O_2$), vinic ether, hydrated butyric acid ($C_8 H_8 O_4$), anhydrous butyric acid, and butyric ether.—[S. S., pages 248 to 252.]

What are vinic acids? and explain the production of ether by the action of alcohol upon sulphovinic acid; and show by means of such reactions why the formula of ether, hitherto in use, must be doubled.—[S. S., pars. 570 and 376 to 391.]

What are monamines, monamides, diamines, diamides, &c.? and explain, by means of symbols, the connection between the following bodies and those just named:—Bimethylamine ($C_4 H_7 N$), acetamide ($C_4 H_5 NO_2$), urea ($C_2 H_4 N_2 O_2$), biethyl urea ($C_{10} H_{12} N_2 O_2$), citramide ($C_{12} H_{11} N_3 O_8$).—[S. S., chap. X.]

Explain what is understood by the terms monatomic, diatomic, and triatomic alcohols, and give an example of each; and show how many classes of ethers may be formed by each with hydrochloric acid.—[S. S., pars. 553, 556, 572, 741, and 841].

Define briefly the following terms:—Allotropism, dimorphism, isomerism, homologous, and isologous series.—[S. S., pars. 191 to 193; 230, and Appendix A, page 278; also F. S., chap. XIII.]

Give a brief definition of the following numerical laws:—1, law of definite proportion; 2, law of multiple proportion; 3, law of equivalents; 4, law of compound proportion; Gay Lussac's law of volume.—[F. S., pars. 126 to 144, and S. S., chap. II.]

Four hundred volumes of a gaseous mixture, consisting of 100 measures of a *carbide of hydrogen* and 300 of oxygen, on being exploded by means of an electric spark, were reduced to 200 volumes. On agitating the residual gas with caustic potash, 100 volumes dissolved, leaving 100 of undissolved pure oxygen—the dissolved gas being carbonic acid, what was the specific gravity of the original carbide of hydrogen, and its formula?

Specific gravity of carbon = 0·846
" " hydrogen = 0·069

—[S. S., Exercise 86, page 72.]

Calculate the formula of an acid body from the following analyses of the hydrated acid and its silver salt :—

	Hydrated acid.	Silver salt, dried at 100° Cent.
C	40·68	14·46
H	5·09	1·20
O	54·23	14·46
Ag O	—	69·88
	100·00	100·00

Equivalent of	Carbon	6
"	Hydrogen	1
"	Oxygen	8
"	Silver	108

—[F. S., chap. XX.]

1863.

Write the formulæ, and give the equivalent volume (of such as can be experimentally determined), compared with that of hydrogen = 2, of the following compounds:—

Compounds of hydrogen with—Br, S, P, O, As, Cl, Te, H, Sb, I, Se, N.

Compounds of oxygen with—S, Br, Se, Te, As, Cl, I, Bo, Si, N, C, P, Sb.

Compounds of chlorine with—S, P, As, Sb.—[S. S., pars. 269 to 271.]

How would you express the composition of the following compounds, by supposing them to be derived from the water type?—Al_2O_3; KO, SO_3; HO, SO_3; SnO_2; HO, NO_5; KO, HO; KO; $3HO, PO_5$; HS.—[S.S., pages 248 to 252.]

Classify the following metals into those which—*a*, decompose water in the cold; *b*, at the temperature of boiling; *c*, at a red heat; *d*, in the cold in the presence of an acid; *e*, at a white heat; and *f*, not at all:—Ca, Bi, Cd, K, Mg, Al, Cu, Hg, Co, Ag, Fe, Au.—[F. S., pages 294 to 297.]

Classify the following oxides into those which—*a*, are reduced to the metallic state by heat alone; *b*, which are not reduced by hydrogen alone; *c*, which are not reduced by charcoal alone:—Cr_2O_3, MnO, Fe_2O_3, ZnO, Al_2O_3 AgO, AuO_3, CuO.—[F. S., pages 294 to 297.]

What do you understand by the terms isomorphism and dimorphism, and allotropism?—[S. S., pars. 243, 230, and 191 to 193.]

What are vinic acids? and explain the theory of etherification.—[S. S., pars. 570 and 376 to 391.]

If the formula of a monobasic alcohol be $C_{2m}H_{2m+2}O_2$, how would you write the formulæ of the following derivatives?—The radical in combination and free; the aldehyde; the monobasic acid with O_4; the biatomic alcohol; the triatomic alcohol; the biatomic acid; the primary monamine base containing the radical; and the urea, or diamine, containing the radical of the biatomic acid.—[S. S., pars. 460 to 462, 563, 735, 761, 834, 973, 1061 to 1063.]

Write the formulæ of the following compounds derived from common alcohol, $C_4H_6O_2$ — sulphide of ethyl (= 4 vol.); tellur-ethyl; the compounds of ether with sulphuric acid, corresponding to neutral and bisulphate of potash (= 4 vol.); acetic ether; iodide of ethyl.—[S. S., pars. 566, 570, 572, 710 to 716, and 825 to 830.]

Write the formulæ of the following fats:—Trichlorhydrine, monochlorhydrine, diacetine, monostearine, trioleine (glycerine, $C_6H_8O_6$; acetic acid, $C_4H_4O_4$; stearic acid, $C_{36}H_{36}O_4$; oleic acid, $C_{36}O_{34}O_4$).—[S. S., pars. 841 to 855.]

What formula would you assign to a salt having the following composition?—

PbO —	83·27	Equivalent of lead	= 104
NO_5 —	13·38	,, oxygen	= 8
HO —	3.35	,, N	= 14
		,, H	= 1

—[F. S., chap. XX.]

ROYAL SCHOOL OF MINES, LONDON.

1862.

Series I.[*]

The formula of nitric acid is HNO_3. What is the composition of nitric acid in 100 parts? $H = 1$; $O = 16$; $N = 14$. Give details of calculation.—[F. S., chap. XIX.]

State the composition of fire-damp and choke-damp in mines.—[F. S., pars. 559 and 555.]

How is benzoic acid converted into benzoic aldehyde? —[S. S., par. 694.]

Express in formulæ the several stages of the action of ammonia upon oxalic ether.—[S. S., par. 827.]

Series II.

A salt has been found to contain, in 100 parts,—

		Equivalents to be used.
Phosphorus	12·65	$P = 31$
Magnesium	9·79	$Mg = 24$
Nitrogen	5·71	$N = 14$
Hydrogen	6·54	$H = 1$
Oxygen	65·31	$O = 16$

What is the formula of the salt? Give details of calculation.—[F. S., chap. XX.]

The formula usually adopted by chemists for felspar is $KO, SiO_3, Al_2O_3, 3 SiO_3$. In this formula $K = 39$: $Al = 13·7$; $Si = 21$; $O = 8$. What is the formula of felspar if the following equivalents are taken?—$K = 39$; $Al = 27·4$; $Si = 28$; $O = 16$. Give details of calculation. —[S. S., page 168, par. 4; par. 884; and F. S., chap. XX.]

A volume, V., of sulphuretted hydrogen is decomposed by an excess of bromine. What is the volume of the resulting hydrobromic acid?—[S. S., page 166, pars. 1 and 2.]

How much oxygen is required for the complete combustion of 100 volumes of a gaseous mixture, consisting of 50 volumes of marsh gas and 50 volumes of olefiant gas? How many volumes of carbonic acid are generated?—[S. S., page 73, Exercises 89 and 90.]

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[*] The student is only permitted to answer eight questions; he may select them from Series I. or II., or from both: the value attached to the correct answer of each question in Series I. is 6, and of those in Series II. is 9.

Give an outline of the manufacture of sulphuric acid.—[F. S., par. 546.]

Give an outline of the manufacture of nitric acid, and state the quantities of sulphuric acid ($H_2 S O_4$), nitrate of potassium ($K N O_3$), or nitrate of sodium ($Na N O_3$), which are required to produce 1 pound of nitric acid ($H N O_3$): $H = 1$; $O = 16$; $N = 14$; $S = 32$; $K = 39$; $Na = 23$.—[F. S., par. 522, chap. XX; and S. S., par. 788.]

Name the more frequently occurring mineral compounds which are insoluble, both in water and acids, and describe the process of rendering them soluble for analysis.—[Q. A., par. 591.]

Calculate the quantities of black oxide of manganese and hydrochloric acid which are necessary to convert respectively into chloroform ($C H Cl_3$), and chloride of carbon ($C Cl_4$), the quantity of marsh gas evolved by the distillation of 1 pound of acetic acid with an excess of lime.—[S. S., par. 637; and F. S., par. 528, and chap. XIX.]

Describe the method of preparing the chlorides of the acid-radicals, and their deportment under the influence of water, alcohol, and ammonia.—[S. S., pars. 927 to 929, and page 422, par. 5.]

The analysis of an organic body, containing carbon, hydrogen, and oxygen, gave the following experimental numbers:—

Substance burnt - -	0·33	$C = 12$
Carbonic acid found -	0·66	$H = 1$
Water found - - -	0·27	$O = 16$

The vapour density of the substance, referred to the density of hydrogen as unity, was found to be 22. What are the composition and formula of the compound? Give details of calculation.—[F. S., chap. XX.; and S.S., pars. 131 to 135.]

Give illustrations of monatomic, diatomic, and triatomic alcohols, and of the aldehydes and acids corresponding to them.—[S. S., pars. 553 to 563, 478, 734 and 760, 834 and 860.]

1863.

Series I.

The formula of natrolite is $Al_2 O_3$, 2 $Si O_2$, Na_2O, $Si O_2$,

$2 H_2O$. Calculate the per-centage composition of this mineral; the following equivalents to be used:—

Hydrogen	= 1
Aluminum	= 27·4
Sodium	= 23
Silicium	= 28
Oxygen	= 16

Give such details as will show the mode of calculation.—[F. S., chap. XIX.]

How many volumes of carbonic acid gas are formed by the combustion of 50 volumes of carbonic oxide?—[S. S., pars. 97 and 98.]

Describe one of the processes for the separation of nickel and cobalt.—[Q. A., par. 167.]

In a nitrogen determination by combustion with soda-lime, 0·223 gramme of substance furnished 0·057 gramme of platinum. What is the per-centage of nitrogen in the compound?—

$$Pt = 197·4 \qquad N = 14$$

—[F. S., chap. XIX.]

Give the composition, properties, and mode of preparation of mercaptan, and state its relation to water and alcohol.—[S. S., par. 366.]

Give the composition of an animal fat, and describe the process of saponification.—[S. S., par. 836.]

Series II.

How much chlorate of potassium is required to obtain 4 litres of oxygen measured at 0° C. and 0·760 metres pressure? One litre of hydrogen at the same temperature and pressure weighs 0·901 grammes. Give such numerical details as will show the method of calculation. [S. S., pars. 1 to 4, and Exercises.]

The per-centage composition of a mineral has been found by analysis to be—

Aluminum	10·81
Silicium	22·10
Calcium	7·89
Hydrogen	2·37
Oxygen	56·83
	100·00

What is the formulæ of the mineral? The following equivalents to be used:—

Aluminum	27·4
Silicium	28
Calcium	40
Hydrogen	1
Oxygen	16

—[S. S., page 168, par. 4, and pars. 883 to 893; and F. S., chap. XX.]

Supposing the whole of the nitrogen contained in 100 volumes of ammonia to be converted, in one case into cyanogen, and in a second case into nitrous oxide, how many volumes of cyanogen and how many volumes of nitrous oxide may be thus obtained?—[F. S., pars. 527 and 526.]

Phosphoretted hydrogen ($H_3 P$) is decomposed by chlorine, so as to yield hydrochloric acid and pentachloride of phosphorus, how many volumes of chlorine are required by 100 volumes of phosphoretted hydrogen, and how many volumes of hydrochloric acid are generated?—[S. S., page 167, par. 3, and page 166, par. 1.]

Describe the composition, properties, and mode of preparation of triethylphosphine.—[S. S., pars. 984 to 988, and Exercise.]

Twenty cubic centimetres of methylic ether ($C_2 H_6 O$) are submitted to combustion. How many cubic centimetres of oxygen are required for its complete combustion? and how many cubic centimetres of carbonic acid are produced?—[S. S., page 73, Exercise 90.]

Give an outline of the principal derivations of ammonia. —[S. S., chap. X.]

The combustion of a liquid has led to the formula $C_4 H_{10} O$. State the alcohol and ethers, simple and mixed, which this formula represents? Again, a liquid has, by analysis, been found to contain $C_4 H_8 O_2$. State the acid and several compound ethers which this formula expresses.—[S. S., page 290, list of alcohols, and pars. 573 and 574; page 306, list of acids, and par. 710.]

METALLURGY.

1862.

Estimate the theoretical maximum calorific intensity of hydrogen and carbonic oxide when burned in oxygen, the specific heat of the vapour of water being 0·475, and the latent heat of steam 537° C., and the specific heat of carbonic acid being 0·2164.—[S. S., par. 1399, and Exercise 205.]

1863.

Suppose three parts by weight of carbonic oxide, and five parts by weight of carbon to be converted into carbonic acid; how much water will the heat thereby developed raise from 1° C. to 100° C.?—[S. S., pars. 1398 to 1401.]

State the number of units of heat which should be produced respectively by the perfect combustion of 10 parts by weight of coal of the following composition:—$C = 85·81$, $H = 5·85$, and $O = 8·34$, and five parts by weight of air—dried wood.—[S. S., pars. 1397 to 1405.]

LONDON UNIVERSITY.

The chemistry papers from the following examination in this university have been selected:—

Matriculation Examination (Pass and Honours).
First and Second B.Sc. Examinations (Pass).
" " " (for Honours).
Examination for the degree of Doctor of Science.

MATRICULATION—PASS EXAMINATION.

1861.

A quantity of oxygen measures 10 cubic inches at 5° C.: required its volume at 60° F., the pressure remaining unaltered.—[S. S., par. 15.]

Explain and exemplify the terms "specific heat" and "latent heat"—[S. S., pars. 43 and 1286.]

Enumerate the compounds which nitrogen forms with oxygen; give the symbol and combining number of each. What action takes place when nitric acid is poured upon copper? Describe the gaseous compound which is then formed.—[F. S., pars. 521, 525; and Ex. 73, page 35.]

What are the components of atmospheric air? Describe the properties of its two most abundant constituents, and state how each may be obtained separately.—[F. S., pars. 520, 519, and 516.]

Describe the preparation, composition, density, and chemical properties of hydrochloric acid.—[F. S., par. 533.]

What is the composition of carbonic acid? How is it obtained in a state of purity? Describe its properties in solid, liquid, and gaseous forms. State its principal natural sources.—[F. S., par. 555.]

A room of 2,000 cubic feet is heated from 60° to 80° F.: how much air is expelled from the room, using Regnault's co-efficient of expansion, viz., $\frac{1}{491}$ of the bulk at 32° for each degree of Fahrenheit's thermometer?—[S. S., pars. 10 to 15.]

What weight of atmospheric air is needed for the complete combustion of 1 lb. of carbon?—[S. S., par. 1400.]

Describe the preparation and properties of nitric acid. Give the tests for its presence.—[F. S., par. 522; and Q. A., par. 473.]

How do you distinguish chemical affinity from other molecular forces?—[F. S., pars. 24 and 126.]

1862.

What are the fixed points from which a thermometer is graduated? State why they have been selected. What degree on Fahrenheit's scale corresponds with 7° C.? and what degree on the Centigrade scale with 70° F.?—[S. S., pars. 1237 to 1252.]

Mention the principal components of the atmosphere, and their relative proportions. How may the presence of each be proved? Describe two of the best methods of obtaining the most active of these constituents.—[F. S., par. 520.]

Give the composition of water by weight and volume. State in words, and describe by symbols, the action of diluted sulphuric acid upon zinc and upon oxide of zinc respectively. Mention the proportions in which each of the substances employed or produced enters into the reaction.—[F. S., par. 518.]

Describe in words, and represent in symbols, the effects of heat upon nitrate of ammonia. Give some account of the chemical properties of the gaseous product.—[F. S., par. 526.]

How is chlorine obtained? Describe its principal properties, and mention the other elements which are allied to it.—[F. S., par. 528; and S. S., par. 270-1.]

What is the action of oil of vitriol upon common table salt? Describe the properties of the products.—[F. S., par. 533.]

At what degree of the Fahrenheit scale does ice melt? and at what degree does water boil? Give the corresponding temperatures of the Centigrade and Reaumur scales.—[S. S., pars. 1246 and 1247.]

What experiment would you arrange in order to ascertain whether a pound of mercury absorbs as much heat as a pound of water, when heated from 40° to 80° F.?—[S. S., par. 1286.]

A room contains 1,000 cubic feet of air: how many cubic feet of oxygen are contained in it? What is the other principal constituent of air? and what is the proportion by weight in which it occurs in the atmosphere? —[S. S., par. 520.]

Describe by symbols the preparation of ammoniacal gas from sal-ammoniac. Enumerate the principal properties of the gas.—[F. S., par. 527.]

MATRICULATION—EXAMINATION FOR HONOURS.

1861.

What volume of carbonic oxide is obtained by reducing 100 cubic centimetres of carbonic acid by red-hot charcoal?—[S. S., par. 97, and Example.]

Describe the formation and properties of the compounds of sulphur and oxygen.—[F. S., pars. 544 to 547.]

Explain what is meant by a degree of temperature on the Fahrenheit's scale, and on the Centigrade scale.—[S. S., pars. 1245 to 1248.]

What would — 220° F. represent in degrees Centigrade? and what 90° Centigrade in degrees Fahrenheit?—[S. S., par. 1254.]

Give an outline of the process for obtaining sulphuric acid, explaining the chemical changes which occur.—[F. S., par. 546.]

How is ammonia prepared in the gaseous and in the liquid state? What are the most common impurities in a solution of ammonia?—[F. S., par. 527.]

Explain what is meant by the terms monobasic, dibasic, and tribasic acids; and give instances of each class. —[S. S., pars. 600 to 610.]

1862.

Describe the action of water upon the following metals, viz.—sodium, iron, and lead, explaining the differences in the effects corresponding to different temperatures.—[F. S., pages 294 and 295.]

How much air is needed for the combustion of a cubic inch of sulphuretted hydrogen?—[F. S., par. 520, and S. S., page 164, par. 2.]

Give the formulæ for the sulphates, nitrates, and carbonates of iron, copper, and lead.—[F. S., pars. 439 to 443.]

Describe the mode of liquefying carbonic acid, chlorine, and ammonia. Mention some of the gases which have not yet been condensed.—[S. S., pars. 21 to 24.]

How much heavier than hydrogen are the following gases and vapours?—Oxygen, nitrogen, steam, carbonic acid, ammonia, chlorine, and bromine.—[S. S., page 586.]

What is the present meaning of the terms acid, base, and salt? What was the theory involved in the terms oxy-acids and hydracids?—[S. S., pars. 600 to 605; 787 to 794; 543 to 546; 706 to 708.]

Suppose a current of electric sparks be maintained through two cubic inches of ammonia, what will be the volume of each of the resulting gases? What volume of oxygen would be required for the combustion of the inflammable constituent?—[F. S., pars. 527 and 518.]

Explain by symbols the action of hydrated nitric acid upon copper. What is the action of heat upon nitrate of ammonia? Give the symbols of the decomposition.—[F. S., pars. 526 and 525, and Exercise 73, page 35.]

FIRST B. Sc. EXAMINATION (PASS).

1861.

Exemplify the difference between a chemical compound and a mechanical mixture, stating in what the difference consists. To which class do an aqueous solution of common salt and a solution of hydrochloric and of sulphuric acid belong?—[F. S., par. 27.]

Suppose 50 cubic feet of marsh gas from a seam of coal to become mixed with 600 cubic feet of air (temp. 60° F., bar. 30 inches), what will be the volume of each of the products at 2000° F. (taking the coefficient of expansion, $\frac{1}{491}$ of the bulk of the gas at 32° for each degree F.), supposing the mixture to explode? and what the volume of the mixture when it has again cooled to the initial temperature?—[S. S., pars. 9 to 16; Exercise 57, page 65; and pars. 97 and 98.]

State what you know on the subject of ozone.—[F. S., par. 516, page 266.]

What are the constituents of gunpowder? To what does it owe its projectile powers? State what you know respecting the products of its combustion.—[S. S., pages 2 and 3.]

A metallic solution is precipitated by hydrochloric acid: what metals might the precipitate contain? and how would you find out which of these is present?—[Q. A., pars. 302 to 307.]

1862.

Mention the elementary bodies allied respectively to chlorine, oxygen, and nitrogen, and state in what points this analogy may be observed.—[S. S., pars. 1, 2, and 3, pages 166 and 167.]

How is a metallic chloride detected in the presence of a metallic iodide?—[Q. A., par. 389.]

When a cubic foot of oxygen combines with carbon, so as to form carbonic acid, what is the volume of the gas? If the quantity of carbon in the gas be doubled, what is the volume of the new gas?—[S. S., pars. 97 and 98.]

For Honours.

1861.

Enumerate the elements which are allied to arsenic; adduce proofs of their resemblance to it, including the chemical characters of their compounds with oxygen and hydrogen.—[S. S., par. 3, page 167.]

A gaseous mixture is believed to consist of hydrogen, nitrogen, and carbonic oxide. How may the presence of these gases be proved, and the quantity of each be ascertained?—[S. S., pars. 156 to 170.]

How would you write the formulæ of nitrate, sulphate, bisulphate, and normal phosphate of potash, upon the binary or salt-radical theory of salts? Sketch the arguments in favour of the binary theory.—[S. S., pars. 219 to 229.]

What do you understand by a chemical equivalent? Illustrate your meaning by examples.—[S. S., pars. 271 to 276.]

How are small quantities of fluorine best detached in insoluble minerals?—[Q. A., pars. 435 to 440.]

Explain the composition of the best known classes of silicates, and give reasons for the formula you use for silica.—[S. S., par. 171; par. 4, page 168; and pars. 883 to 893.]

Describe the allotropic modifications of sulphur, and state how each of them is prepared.—[S. S., par. 192.]

1862.

What is meant by the term "isomorphism"? Exemplify it in two or three distinct cases. What is the process of purifying alum from iron? Explain the theory of this process.—[S. S., pars 243 to 252.]

Define the term, "chemical equivalent," and illustrate it by examples. What evidence is there that nitrogen has, in some compounds, a different equivalent value from that which it has in others?—[S. S., pars. 271 and 272, and 438 to 446.]

What are the tests for nitric acid? Explain the reactions by symbols.—[Q. A., pars. 473 to 476.]

How do you prepare hydrochloric and hydriodic acids, both in the gaseous form and in solution? Describe the preparation of a solution of chloric and one of iodic acid. Illustrate the difference of the affinities of chlorine and iodine for oxygen and hydrogen, as shown in the formation and properties of their several compounds.—[F. S., pars. 528 to 534, and 538 to 541.]

Give the empirical and rational formulæ for the following substances:—Sulphuric, nitric, oxalic, phosphoric, boracic, carbonic, and sulphurous acids, and each of the potash salts which they form.—[F. S., par. 426; and S. S., pars. 600 to 612, 787 to 795, 812, and 871 to 878.]

Give the formulæ and chief properties of the compounds which phosphorus forms with oxygen and hydrogen—[F. S., pars. 550 to 553.]

Describe three of the simplest compounds of carbon and hydrogen, and the mode of preparing them. What are their respective densities compared with hydrogen? What is the action of chlorine upon each?—[S. S., pars. 521 to 526.]

How is chloride of silicon obtained? Give the density of its vapour compared with hydrogen. What assistance does this datum afford in fixing the atomic weight of silicon?—[S. S., par. 171, and pages 168 and 587.]

SECOND B. Sc. EXAMINATION (PASS).

1861.

Describe the method of preparing cyanogen, and mention its principal properties.—[F. S., par. 562.]

How much oxygen is required for the combustion of one cubic inch of cyanogen? What would be the volume of the resultant gases at the initial temperature and pressure?—[S. S., pars. 97 and 98.]

Explain what is meant by the law of substitution. State the action of chlorine upon acetic acid and upon olefiant gas.—[F. S., par. 397, and S. S., pars. 517 and 632.]

Give an account of the mode of preparing cyanuric acid. What bodies are isomeric with it? Which of them can be formed from it, and how?—[F. S., pars. 391 to 396.]

Distinguish between simple and compound ethers. State how a double or mixed ether may be obtained. State the action of oxalic acid upon alcohol.—[S. S., pars. 555, and 384 to 387.]

Describe the principal modes of forming ammonias containing ethyl. Classify the different varieties of ammonia so obtained.—[S. S., pars. 973 to 979.]

What are the characteristics of an alcohol? Mention some of the most important members of the alcohol series, and give their formulæ. In what respect does the first term of the series differ from the others?—[S. S., pars. 553 to 560.]

Describe the mode of determining the vapour density of ether by Dumas's method.—[S. S., 128 to 131.]

1862.

A volatile organic liquid, composed of carbon, hydrogen, and oxygen, was burnt with oxide of copper; 0·430 grm. gave 1·249 grm. of carbonic acid and 0·219 grm. of water: calculate the empirical formula of the compound, and give any suggestions which occur to you for the discovery of its rational formula.—[F. S., chap. XX.]

Describe the action of chlorine on olefiant gas, and contrast it with the action of chlorine on chloride of ethyl. —[S. S., pars. 525 and 906.]

Describe the formation and properties of some hydrocarbons homologous with olefiant gas. How is the molecular weight of each of them ascertained?—[S. S., pars. 521 to 525, and Appendix A, page 278.]

Describe the two commonest homologues of alcohol. How may each of them be obtained in a pure state?—[S. S., pars. 559 to 561.]

Describe the products of the distillation of acetate of potash. What products are formed when the salt is distilled with hydrate of barytes?—[S. S., pars. 508 and 693.]

Describe the preparation of pure citric acid. How is it distinguished from tartaric acid?—[Q. A., par. 504.]

For Honours.

1861.

Five grains of an organic acid yield, on combustion with oxide of copper, 3·001 grains of water and 7·33 of carbonic acid: calculate its empirical composition, and state how you would attempt to determine its molecular weight.—[F. S., chap. XX.]

What compound radicals are supposed to exist in vinic alcohol, acetic acid, and succinic acid? How may the chlorides of these radicals be obtained? What is the action of these chlorides upon dry benzoate of potash?—[S. S., pars. 386, 391 to 395, and 812.]

Give an example of the formation of a diatomic alcohol, and state what is its vapour volume as compared with that of hydrogen.—[S. S., par. 734.]

What are the products of the gradual action of oxygen upon common alcohol? How are these products obtained in a state of purity?—[S. S., par. 563.]

How may acetone, marsh gas, methyl, and cyanide of methyl be respectively obtained from acetic acid?—[S. S., pars. 508, 637, 466, and 912.]

What is meant by an anhydride? How may nitric, sulphuric, acetic, and succinic anhydrides be severally obtained?—[S. S., pars. 391 to 395, and 793.]

How are two distinct alcohol radicals made to enter simultaneously into the composition of an ether? What light does the formation of such bodies throw upon the molecular constitution of common ether?—[S. S., pars. 384 to 387.]

What is the chemical constitution of glycerine, and to what class of bodies does it belong? How is it obtained in a state of purity?—[S. S., par. 834.]

1862.

Classify the best known chemical elements under the heads of monatomic, diatomic, and triatomic elements. Give formulæ of some of their characteristic compounds which support this classification.—[S. S., par. 270, and Appendix B, page 279.]

Define what is meant by the molecular weight of a compound, and distinguish it from its equivalent or combining proportion, illustrating your view by means of sulphuric, citric, phosphoric, and nitric acids.—[S. S., chap. III.]

Describe the mode of preparing aceto-benzoic anhydride. What is the action of chloride of benzoyl on succinate of potash?—[S. S., par. 394.]

How is lactic acid usually procured? How is it obtained from aldehyde? In what relation does it stand to propionic acid?—[S. S., pars. 805, 490, and 810.]

What is the action of heat upon the neutral and upon the acid oxalate of ammonia? What is implied by the term "imide?" Give an example of its formation.—[S. S., pars. 1003 and 997—4.]

Doctor of Science.

1862.

Show the mode of applying the law of volumes to the determination of atomic weights. Illustrate its value as a means of classifying both elementary and compound substances. Mention some of the most important cases of anomalous vapour density. What explanation of these anomalies may be suggested?—[S. S., pars. 113 to 123, and 334 to 338.]

0·31 gram. of an organic acid yields, on combustion, 0·62 gram. carbonic acid and 0·2536 gram. water: give the empirical formula of the acid.—[F. S., chap. XX.]

Sketch the chemical history of malic, tartaric, and succinic acids, and their relations one to another.—[S. S., pars. 817 to 821.]

Contrast the oxidized derivatives of vinic alcohol and glycol, giving their composition, properties, and mode of preparation.—[S. S., pars. 755 to 757, and 761.]

Give a history of the progress of discovery of the various methods by which the artificial organic bases and amides are produced.—[S. S., pars. 408 to 418, and chap. X.]

Describe the principal organo-metallic bodies which contain arsenic, and give a theory of their constitution.—[S. S., pars. 1151 to 1155.]

Give the formulæ for silicic and boracic acids, and your reasons for selecting the particular formulæ which you adopt. Classify the principal silicates and borates, giving examples.—[S. S., par. 171, and par. 4, page 168, and pars. 883 to 893.]

How is heat of combustion estimated? Mention some of the principal obstacles to an accurate comparison of the results furnished by the different elements.—[S. S., pars. 1335 to 1397.]

What is the density of a vapour, taken by the method of Dumas, under the following conditions:—

Weight of globe full of vapour	10·689 gram.
Weight of globe full of dry air at 15° C.	10·534 „
Temperature at sealing	130° C.
Barometer at sealing	30 inches
Capacity of globe	151 cub. cent.
Air retained (at 15° C.)	0·5 c. c.

the expansion of the glass by heat being neglected?—[S. S., pars. 129 to 131.]

TRINITY COLLEGE, DUBLIN.

Experimental and Natural Science Moderatorship.

1861.

Organic Chemistry.

Describe two known processes for preparing potassium alcohol, and the manner in which it should be treated with a view to the formation of $C_2 H_5 O$, $C_{10} H_{11} O$.—[S. S., pars. 565, and 384 to 390.]

Explain the methods of making the methyl and ethyl hydrocyanic ethers, and the products into which these compounds are converted when they are heated in contact with a concentrated alcoholic solution of potash.—[S. S., pars. 912, 913.]

By the action of ammonia in different ways on oxalic ether two distinct compounds may be obtained: name these compounds, and explain the manner in which each is produced.—[S. S., par. 827.]

What is the simplest process for preparing the oxalovinate of potash?—[S. S., par. 828, and Exercise 156.]

How is chloral made? What is its formula, and what the results of the action upon it of an alcoholic solution of potash?—[S. S., par. 784.]

Explain Gerhardt's method for preparing the acetic and benzoic anhydrides.—[S. S., pars. 391 to 395.]

From the terbromide of allyl glycerine may be artificially made: what are the successive steps of the process, and what the formula of the product?—[S. S., pars. 954 and 838.]

Write the formula of allylic alcohol, and state how it is made. Mention also the composition of acroleine, and its position in the allylic series.—[S. S., pars. 579, 580, 493.]

What are the conclusions at which Kolbe arrives in relation to the proximate constituents of valerianic acid, and which he deduces from the results of its electrolysis? —[S. S., par. 625.]

Where is hippuric acid found, and how is it insulated? Write its formula, and state also the proximate constituents of which it is composed.—[S. S., pars. 808 and 809.]

Write the formula of aniline, and explain the mode of preparing it from phenyl alcohol, from nitrobenzol, and from indigo.—[S. S., pars. 593, 475, 973, and 989.]

Explain the mode of procuring the hydrated oxide of methyl-ethyl-amyl-phenyl ammonium.—[S. S., pars. 977 to 980, and 547 to 552.]

An unknown organic acid, not including any nitrogen, was combined with oxide of silver, and upon the salt thus formed the following experiments were made:—

I. 50 grains when ignited left 35·29 metallic silver.

II. 30·6 of it when burned gave 3·8 carbonic acid and 0·2 water.

From these data deduce the composition of the acid, on the hypothesis of its being monobasic.—[F. S., chap. XX.]

7·33 grains of a liquid, burned with oxide of copper, gave 14·66 of carbonic acid and 6 of water; the density of its vapour also was 3·04. From these data, and from the assumption that the condensation of the vapour is to 4 volumes, calculate the formula which represents the liquid. —[F. S., chap. XX.; and S. S., pars. 131 to 136.]

Write the formula which should be employed in determining, by Dumas's method, the specific gravity of a vapour.—[S. S., par. 130.]

Give the formula of ethylamine urea, and explain the two processes by one or the other of which it may be made.—[S. S., pars. 1059 to 1063.]

Mineral Chemistry.

Write, according to the unitary system, the formula of common phosphate of soda.—[S. S., par. 872.]

One hundred volumes of a mixture of marsh gas, hydrogen, carbonic oxide, and nitrogen, mixed with 150 volumes of oxygen, were subjected, in a eudiometer, to the action of the electric spark, and the diminution of volume found to be 151·5 volumes. The residual gas, by exposure to potash, underwent a further diminution, amounting to 37 volumes. Lastly, the gas which remained was exploded by the spark, after mixture with at least twice its volume of hydrogen, and the reduction of volume which ensued was 22·5 volumes. From these data deduce the composition of the mixture.—[S. S., pars. 156 to 169.]

1862.

If *a* represents in grains weight the per-centage of carbon in an organic compound, and *v* and *v′* be the relative volumes of carbonic acid and nitrogen, obtained by burning it with oxide of copper, what will be the per-centage weight of the nitrogen?—[S. S., pars. 82 and 83, and Exercises 39 and 40.]

Write the composition of alanine; describe the mode of making it; mention the compounds with which it is isomeric, and how it may be converted into lactic acid.—[S. S., par. 490.]

What are the two reasons usually assigned for doubling the ordinary formula for oxide of ethyl, and the substances which occur in the same homologous series with it?—[S. S., pars. 384 to 391.]

Explain the action of a solution of caustic potash on cyanide of ethyl and cyanate of oxide of ethyl.—[S. S., pars. 913 and 410.]

Give the formula of propionic acid, and the different processes by which it may be artificially made.—[S. S., pars. 620, 629, 631, and 810.]

Write the formula of ethylene alcohol, and explain how it may be obtained.—[S. S., pars. 734 to 738.]

Write the empirical formula of glycerine, and its formula also on the supposition of its being a triatomic alcohol, and explain how it may be formed artificially.—[S. S., pars. 834 to 840.]

What are the experiments, and what the calculations, which enable the chemist to assign the quantities of hydrogen, marsh gas, and carbonic oxide in a mixture of such gases?—[S. S., pars. 156 to 169.]

Sheerer analysed a mineral with the following results:—

Silex - - - - - -	43·70
Alumina - - - - - -	32·31
Peroxide of iron - - - -	1·07
Lime - - - - - -	0·84
Soda - - - - - -	15·83
Potash - - - - - -	5·60

Give its empirical formula.—[F. S., chap. XX., and S. S., pars. 255 to 259.]

QUEEN'S COLLEGE, BELFAST.

1861.

Faculty of Medicine.

Explain by symbols the reactions which take place when oxygen gas is prepared by the action of heat on $Mn\,O_2$ and $K\,O, Cl\,O_5$.—[F. S., par. 516.]

Describe the principal reactions of ozone, and the conditions under which it is formed.—[F. S., par. 516.]

Give a particular description of the method of analysing atmospheric air by means of hydrogen gas.—[S. S., pars. 156 to 170.]

What bodies have been found in atmospheric air besides oxygen, nitrogen, and carbonic acid?—[F. S., par. 520.]

Give some account of hydrocyanic acid, its preparation, properties, and tests.—[F. S., par. 563.]

What is the composition of gunpowder, and the principal products which are formed when it explodes?—S. S., page 2, Exercise 9.]

If $C = 12$, $H = 1$, $N = 14$, $O = 16$, $Cl = 35{\cdot}5$, $K = 39$, what are the formulæ of the following bodies?—Water, hydrochloric acid, alcohol, ether, nitrate of potash.—[S. S., pars. 113 to 122, and pages 248 to 251.]

What are the four types to which Gerhardt refers organic compounds? Illustrate them by writing the formulæ, according to this view, of methyl, ethyl, marsh gas, wood spirit, alcohol, hydrochloric ether, and ethylamine.—[S. S., pars. 426 and 427, and pages 248 to 251.]

If a given quantity of gas in the moist state, at the temperature of 10° C., and under a pressure of 28 inches, measure 150 cubic inches, what volume would it occupy in the dry state at 0° C., and under a pressure of 30 inches (tension of watery vapour at 10° C., 0·36 inches; coefficient of expansion for 1° C., 0·00366)?—[S. S., pars. 5 to 83.]

How is the latent heat of water determined?—[S. S., par. 43.]

Describe the method usually employed by chemists to take the densities of vapours, and state how it has been recently applied to the determination of vapour densities at very high temperatures.—[S. S., pars. 123 to 128.]

What are the effects produced by an electrical current when traversing an electrolyte?—[F. S., par. 345.]

ENGINEERING SCHOLARSHIPS.

Second Year's Students.

If a given quantity of air measure 140 vol. at 10° C., and under a pressure of 29·7 inches, what volume will it occupy at 0° C., and under a pressure of 30 inches?—[S. S., page 3, pars. 5 to 43.]

How is the tension of a vapour determined?—[S. S., pars. 66 to 73.]

Give some account of the methods of preparing, and of the properties of ozone.—[F. S., par. 516.]

Describe the different methods which are known of reducing the condensable gases to the liquid state.—[S. S., pars. 21 to 24.]

Change, where necessary, the commonly received atomic weights of the following bodies, so that in every instance one volume of each body may correspond to one atom, viz.:—Hydrogen, oxygen, nitrogen, sulphur, chlorine.—[S. S., pars. 113 to 116.]

Give a full account of the theory of volumes.—[S. S., pars. 84 to 122.]

Describe the different modes of preparation, and the properties of sulphurous acid.—[F. S., par. 545.]

Describe fully the tests of hydrocyanic acid; state also its composition, and the mode of preparing it.—[Q. A., par. 381, and F. S., par. 563.]

Enumerate the more important metals, and arrange them in classes, according to their chemical properties.—[F. S., chap. XXIII.]

What are the compounds which arsenic forms with oxygen and sulphur? State their composition and describe their properties.—[Q. A., pars. 263, 264, and 285.]

Mention the more important alkaloids, natural as well as artificial, which do not contain oxygen. Describe their general properties, and the sources from which they are derived.—[S. S., pars. 972 to 983.]

MEDICAL SCHOLARSHIPS.

Practical Chemistry.

Describe the methods of determining the density of a solid body, and state the precautions required in order to obtain accurate results.—[F. S., pars. 113 to 116.]

What are the distinctive properties of the salts of potassa and soda?—[Q. A., pars. 112 and 114.]

What are the blowpipe reactions of the salts of cobalt, magnesia, and copper?—[Q. A., pars. 108, 162, and 332.]

THIRD YEAR ARTS AND FIRST YEAR MEDICINE AND ENGINEERING STUDENTS.

1862.

What are the different states of matter? Describe them, and the conditions under which bodies pass from one state to another.—[F. S., pars. 3, 4, and 5.]

In graduating a mercurial thermometer, what are the chief points requiring attention in order to secure an accurate instrument?—[S. S., pars. 1235 to 1254.]

Describe the method of correcting a dry gas for temperature and pressure.—[S. S., pars. 12 to 15, and 42.]

What are the circumstances which influence the boiling point of a liquid?—[S. S., pars. 49 to 52.]

Mention the principal gases which have been liquefied, and describe the methods by which their liquefaction has been effected.—[S. S., pars. 21 to 24.]

Describe the method of determining the latent heat of steam, and state how it is affected by the temperature at which the vapour is formed.—[S. S., par. 58.]

How is nitrogen gas prepared? and under what conditions will it combine with the following elements, viz.—Hydrogen, oxygen, and carbon?—[F. S., pars. 519 and 209 to 211.]

What is the supposed composition of ammonium? State also the reasons for assuming the possible existence of such a compound.—[S. S., pars. 398 to 401, and 417.]

Give the composition, by weight and by volume, of the following compounds:—Water, ammonia, deutoxide of nitrogen, hydrochloric acid, carbonic oxide, marsh gas, olefiant gas ($H = 1$; $O = 8$; $N = 14$; $Cl = 35·5$; $C = 6$). —[F. S., pars. 518, 527, 525, and 533.]

Mention some of the natural groups under which certain elements may be classed, and the leading properties of each group.—[S. S., pars. 269 to 271.]

What are the sources and properties of iodine, and how is it prepared?—[F. S., par. 538.]

Describe the solar spectrum, and contrast it with the spectra of the following metals:—Sodium, lithium, strontium.—[S. S., pars. 1539 and 1540.]

What are the distinguishing tests of baryta, lime, and magnesia, respectively?—[Q. A., par. 137, page 55, par. F 4, and par. 160.]

Mention the more important acids of the form C_{2n}. H_{2n}, O_4, and state how they can be derived from their respective alcohols.—[S. S., page 306, par. 620.]

ENGINEERING SCHOLARSHIPS.

Second Year Students.

The atomic weights of copper, lead, and mercury being 32, 104, and 100, respectively, and the specific heat of copper 0·095, calculate, according to the law of Dulong and Petit, the specific heats of lead and mercury.—[S. S., pars. 1286 to 1301.]

Contrast the appearances presented by the solar spectrum with the spectra produced by the metals sodium and lithium, or their salts.—[S. S., pars. 1539 and 1540.]

State the composition and describe the methods of analysing atmospheric air.—[F. S., par. 520.]

Give an account of the preparation and chief properties of phosphoric acid.—[F. S., par. 551.]

Name C_2NH, and describe its properties and tests.—[Q. A., pars. 449 to 455.]

What are the sources of light carburetted hydrogen; how is it prepared artificially? State also how many volumes of oxygen are required for its complete combustion, and how many volumes of carbonic acid and of aqueous vapour are formed.—[F. S., par. 559, and S. S., chap. II.]

Describe the preparation and properties of carbonic oxide.—[F. S., par. 556.]

What are the characteristic tests of potash and soda?—[Q. A., pars. 112 and 114.]

State the composition of common alum. Give also the formulæ for the other alums of analogous composition.—[Note, page 146, S. S.]

Describe the method of separating silica from a silicous mineral which is not attacked by acids.—[Q. A., par. 444.]

Give an account of the method of taking the density of a vapour, and show how the density will serve to control the results of analysis.—[S. S., pars. 123 to 135.]

What is the composition of tartaric acid; its relations to racemic acid; and how is it prepared artificially?—[S. S., par. 820.]

Mention the principal acids of the form $C_{2n} H_{2n} O_4$, and state their relations to the alcohols.—[S. S., pars. 620 and 563.]

What relation has been observed in certain organic bodies between their boiling points and atomic constitution?—[S. S., pars. 1261—1278.]

FACULTY OF MEDICINE.

Practical Chemistry.

What are the blowpipe tests of the following bases?—Potash, soda, alumina, oxide of manganese, and oxide of cobalt.—[Q. A., pars. 112, 114, 195, 171, and 180.]

QUEEN'S COLLEGE, CORK.

Pass Questions.

1861.

What is the law of multiple proportions? Give an example.—[F. S., par. 142.]

What are oxacids and hydracids? Represent by symbols, sulphurous, nitric, perchloric, hyposulphuric, and phosphoric acids as hydracids.—[F. S., par. 426, and S. S., par. 219.]

Give the preparation and the properties of chlorine.—[F. S., par. 528.]

How is phosphorus prepared in its ordinary and in its allotropic forms? State the properties of these two forms.—[F. S., par. 549, and S. S., pars. 191 and 192.]

What are the tests for NO_5, SO_3, PO_5, and HCy?—[Q. A., pars. 392, 383, 385, and 381.]

What are the tests for salts of manganese, iron, copper, bismuth, and antimony?—[Q. A., pars. 171, 202, 204, 330, 324, 256.]

1862.

Write the symbols of sulphide and chloride of potassium, sulphite, hyposulphite, nitrite of potash, and sulphate and chlorate of potash.—[F. S., pars. 439 to 443.]

Give the formulæ of the oxygen compounds of chlorine; and state how hypochlorous acid is formed.—[F. S., pars. 529 and 530.]

Give the preparation and the properties of protoxide and binoxide of nitrogen.—[F. S., pars. 525 and 526.]

What are the tests for HI, HCy, NO_5, and SO_3?—[Q. A., pars. 391, 381, 392, and 383.]

How is ammonia prepared? Give its composition and properties.—[F. S., par. 527.]

What is meant by single and double elective affinity? Illustrate by examples.—[F. S., pars. 168, 169, 182, and 183.]

What is the composition of the atmosphere? By what means is its uniformity in composition maintained?—[F. S., pars. 520 and 177.]

What are the tests for the salts of baryta, alumina, iron, copper, and mercury?—[Q. A., page 55, par. D 1, pars. 195, 201, 205, 330, and 321.]

Give the laws of combination.—[F. S., pars. 126 to 143.]

Prize Questions.

1861.

How many grains of $Ba, Cl + 2HO$ are required to precipitate all the sulphuric acid in twenty grains of $NaO\,SO_3 + 10HO$?

$Ba = 68{\cdot}5$ | $Cl = 35{\cdot}5$
$Na = 23{\cdot}0$ |

—[F. S., chaps. XIX. and XX.]

Give in symbols the ethers, alcohols, aldehydes, and acids of the methylic and ethylic series.—[S. S., pars. 559, 563, 573, 483, and 616.]

State the mode of preparing and the properties of the anhydrous and hydrated hydrocyanic acids.—[F. S., par. 563.]

1862.

Explain the law of combination by volumes.—[S. S., pars. 84 to 97.]

What is meant by allotropy? How are the allotropic forms of oxygen and phosphorus produced? Give the properties of these two elements in their allotropic and in their ordinary condition.—[S. S., pars. 191 to 193; F. S., par. 516.]

Give the preparation and the properties of I and of H I.—[F. S., pars. 538 and 540.]

Give the preparation, the properties, and the composition, by weight and by volume, of nitric and hydrochloric acid.—[F. S., pars. 522 and 533.]

Give the formulæ of the oxygen compounds of phosphorus; and state the mode of preparation, the properties, and the tests of phosphoric acid.—[F. S., pars. 550 and 551; and Q. A., par. 385.]

Explain the binary theory of salts.—[S. S., pars. 219 to 229.]

How has Graham shown that many basic salts can be regarded as really neutral salts?—[S. S., par. 1516.]

Six grains of an organic substance, containing C, H, O, give, on combustion with oxide of copper, 8·8 grains of $C\,O_2$, and 4·2 of $H\,O$; calculate its per-centage composition.—[F. S., chap. XIX.]

SENIOR SCHOLARSHIP IN ARTS OF FOURTH YEAR.

1861.

In what proportions, by volume, do N and O unite to form protoxide and binoxide of nitrogen and hyponitric acid? Calculate the specific gravity of the three compounds.

$$\begin{aligned}\text{Sp. gr. of } N &= 0{\cdot}9713\\ O &= 1{\cdot}1056\end{aligned}$$

—[F. S., pars. 523, 525, 526, and S. S., par. 136.]

How is the combining volume of a gas calculated? What is the ultimate reason of the law of combination by volume?—[S. S., pars. 84 to 106.]

Explain the binary theory of salts.—[S. S., pars. 219 to 229.]

Give examples and state the nature of ammonium, ammonia, and nitrile compounds in organic chemistry.—[S. S., pars. 962 to 973, and 547 to 551.]

How are the compound ethers generally prepared?—[S. S., par. 714.]

Explain in symbols the action of concentrated mineral acids on hydrated hydrocyanic acid.—[F. S., par. 563.]

The double salt of morphia and platinum yields, on combustion, 20·14 parts of metallic platinum; calculate the atomic weight of morphia.

$$Cl = 35{\cdot}5 \qquad Pt = 99{\cdot}$$

—[F. S., pars. 476 to 479.]

SCHOLARSHIPS IN ARTS, MEDICINE, AND ENGINEERING.

1861.

Give examples, by formulæ, of simple and double decomposition.—[F. S., chap. XVIII.]

Explain shortly the atomic theory.—[F. S., pars. 138 to 140.]

In what manner is iodine prepared? What are its properties?—[F. S., par. 538.]

Give the number of volumes which unite, and the condensation which takes place, when N and H form ammonia, and N and O form protoxide and binoxide of nitrogen and hyponitric acid.—[F. S., pars. 527, 526, and 525.]

What is a compound radical? Give examples.—[S. S., par. 194.]

How is urea artificially prepared?—[S. S., par. 1060.]

SCHOLARSHIPS IN ARTS, ENGINEERING, AND AGRICULTURE.

1862.

What are the laws of combination?—[F. S., pars. 126 to 149.]

How is ozone prepared, and what are the points of difference between its properties and those of ordinary oxygen?—[S. S., par. 193.]

How is phosphoric acid prepared?—[F. S., par. 551.]

What are the tests for hydriodic, nitric, carbonic, and sulphuric acids?—[Q. A., pars. 391, 392, 379, and 383.]

What are the two modifications of silicic acid; and how are they converted into each other?—[Q. A., par. 440.]

What is a salt radical? Give examples of simple and compound salt radicals.—[S. S., pars. 219 to 221.]

What are the tests for alumina, zinc, lead, potash, and ammonia?—[Q. A., pars. 195, 174, 313, 314, 106, and 112.]

How many grains of nitrate of silver are required to decompose ten grains of chloride of sodium?—

$$Ag = 108 \qquad Na = 23 \qquad Cl = 35{\cdot}5$$

—[F.S., chap. XIX.]

SCHOLARSHIPS OF THE SECOND YEAR IN MEDICINE.

What is the law of equivalents?—[F. S., pars 136, 137; and S. S., par. 271.]

Explain the law of combination by volume.—[S. S., chap. II.]

How is the amalgam prepared in which $N H_4$ is supposed to exist?—[S. S., pars. 399 and 400.]

What are the tests for $H I$, $H Cy$, $N O_5$, and $P O_5$?—[Q. A., pars. 391, 381, 392, and 385.]

Give the preparation and the properties of $N O$ and $N O_2$.—[F. S., pars. 525 and 526.]

What are the reactions which take place in preparing $N O_5$ from equal weights of nitre and oil of vitriol? Why is $N O_5$ more easily obtained by those proportions than when a smaller quantity of oil of vitriol is employed?—[F. S., par. 522.]

Salts of silver, peroxide of mercury, zinc, and lime are in the same solution: separate them, and give the characteristic reagent for each.—[Q. A., table VII., page 134, pars. 1, 2, 4, and 5; and pars. 319, 174; and page 55, par. F. 4.]

How many grains of nitrate of silver are required to precipitate four grains of $H Cy$?

$$Ag = 108 \qquad C = 6$$

—[F. S., chap. XIX.]

SENIOR SCHOLARSHIPS IN ARTS OF THE FOURTH YEAR.

Explain the constitution of salts on the salt radical theory.—[S. S., pars. 219 to 228.]

How is HI prepared? and why cannot a process be adopted similar to that followed in the formation of HCl? —[F. S., par. 540.]

One ounce of HO, NO_5 is wanted: how much nitre and HO, SO_3 are required, by theory, for the reaction, so as to leave bisulphate of potash in the retort?

$$K = 39$$

—[F. S., chap. XIX.]

Give the formula, mode of preparation, and properties of the aldehyde of the ethylic series.—[S. S., pars. 483 to 485.]

Calculate the formula of hydrated acetic acid from the following data:—100 grains of acetate of silver on combustion gave—

$$\begin{array}{rl@{\qquad\qquad}rl} C = & 14{\cdot}37 & & \\ H = & 1{\cdot}80 & & \\ O = & 14{\cdot}37 & C = & 6 \\ Ag\,O = & \underline{69{\cdot}46} & Ag = & 108 \\ & 100{\cdot}00 & & \end{array}$$

—[F. S., chap. XX.]

QUEEN'S UNIVERSITY IN IRELAND.

1861.*

B.A.—PASS EXAMINATION.

State the points in which chemical affinity and cohesion agree and differ from each other, and mention the circumstances which may modify the former.—[F. S., pars. 23 and 24, 123 to 127, 193 and 194.]

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* At the time of going to press the examination papers for 1862 were not published.

Explain the law of multiple proportions. Give examples in symbols.—[F. S., pars. 142 and 143.]

Explain the doctrine of isomorphism. Give examples in symbols of isomorphous groups.—[S. S., pars. 243, 246 to 250, and 255 to 260.]

What are the different processes for preparing chlorine, and to what uses in the arts is it applied?—[F. S., pars. 528 and 530.]

Give the preparation, the properties, the composition by weight and by volume, and the combining volumes, of sulphurous and of hydrochloric acids.—[F. S., pars. 533 and 545; and S. S., pars. 1 and 2, page 166.]

How many cubic inches of oxygen can be obtained from 100 grains of chlorate of potash?

$$K = 39 \qquad Cl = 35{\cdot}5$$

At 60° Fahr., and 30° bar., 100 cubic inches of oxygen weigh 34·29 grains.—[S. S., pars. 1 to 5.]

Give the preparation, properties, and uses of $NaO\,S_2\,O_2$.—[F. S., par. 547.]

Give the preparation and properties of cyanogen.—[F. S., par. 562.]

How is the atomic weight of an organic acid ascertained? Calculate the atomic weight of acetic acid from the following data:—10 grains of acetate of silver leave, on combustion, 6·467 grains of metallic silver.

$$Ag = 108.$$

—[F. S., pars. 476 to 481.]

WITH HONOURS.

The laws of combination, and the doctrine of equivalents, have been explained by Dalton's atomic theory: explain this theory, and point out the difficulties to its complete adoption, in its original form, when applied to the combination of gases.—[F. S., pars. 138 to 144.]

What are saline and crystalline water? Illustrate these in the rational formula of sulphate of magnesia, and explain the part the former plays when this salt crystallizes from the same solution with sulphate of potash.—[S. S., page 151.]

Explain the salt radical theory, and state the arguments for and against this theory.—[S. S., pars. 219 to 229.]

Give the mode of preparation, the properties, and the composition, in weight and in volume, of protoxide and of binoxide of nitrogen, and of hyponitric acid. Calculate the specific gravity of the three compounds.

Specific gravity of N = 0·972
" " of O = 1·1057

—[F. S., pars. 523, 525, and 526.]

Ascertain the rational formula of the following compound from its per-centage composition:—

$$\begin{aligned} NaO &= 25{\cdot}96 \\ SO_3 &= 66{\cdot}55 \\ HO &= 7{\cdot}49 \\ \hline & 100{\cdot}00 \end{aligned}$$

Equivalent of Na = 23

—[F. S., pars. 476 to 481.]

Write, according to the oxygen acid theory of salts, the formulæ of neutral, acid, and basic salts of sulphuric, tartaric, and ordinary phosphoric acid, with protoxide and with sesquioxide of iron. Give the reasons for such formulæ.—[F. S., pars. 445 to 451.]

The double salt of morphia and platinum yields, on combustion, 20·14 parts of metallic platinum: calculate the atomic weight of morphia.

Cl = 35·5 Pt = 99

—[F. S., pars. 445 to 451.]

What are the present views of the nature of the compound ammonias? Explain the mode of preparation and the properties of ethylamine.—[S. S., pars. 962 to 974.]

Give the mode of preparation and the properties of $C_4H_4O_2$. Mention to what homologous series it belongs; and state, generally, what are the characteristics of homologous series.—[S.S., par. 483; and Appendix A, page 278.]

M.A. Degree.

In the formation of HS, HCl, NH_3, NO_4, how many volumes of the different elements unite; and what is the number of volumes of the resulting compound in each case?—[S. S., par. 270.]

Give the preparation, properties, and the composition, by weight and by volume, of hypochlorous acid. How is its most important compound with lime prepared on the large scale for the arts?—[F. S., par. 530.]

Define the terms monobasic, bibasic, and tribasic acids. Give examples, in symbols, on the salt radical theory, of the neutral salts of these acids with potash and with sesquioxide of iron.—[S. S., pars. 219 to 229.]

Explain the nature of double salts, and the mode of their formation in the magnesian family.—[S. S., page 151.]

How much $PbO, \bar{A}, 3HO$, and $NaOSO_3, 10HO$ are to be mixed together to produce 10 lbs. of anhydrous acetate of soda?

$$Pb = 103 \qquad Na = 23$$

—[F. S., chap. XIX.]

M.D. EXAMINATION, WITH HONOURS.

What is meant by the allotropic forms of bodies? State the properties of oxygen in its ordinary and in its allotropic forms, and mention some of the means by which the latter state is produced, and how its presence is detected.—[S. S., pars. 191, 192, and 193; F. S., page 266.]

Explain the law of equivalents. Illustrate it in the preparation of 1,000 grains of nitric acid, on the supposition that sulphuric and nitric acids are both monobasic monohydrates, and the residue in the retort is bisulphate of potash.

$$K = 39$$

—[F. S., pars. 136 and 137.]

How do you judge of the neutrality of the salt of a bibasic acid on the oxygen theory of salts? Illustrate this in the case of Rochelle salt and of tartar emetic.—[F. S., pars. 445 and 446.]

What is meant by homologous series? To what homologous series does valerianic acid belong? Give its formula, and the process for preparing it.—[S. S., Appendix A, page 278, and par. 620.]

Give the formulæ of the alcohols, ethers, aldehydes, and acids of the first five members of the homologous series.

$$C_n H_{n+1}$$

—[S. S., pars. 559, 563, and 573.]

M.D. EXAMINATION.

Explain the doctrine of multiple proportions; illustrate by examples in symbols.—[F. S., pars. 142 and 143.]

What is the law which gases follow in combining? Illustrate this in the formation of water, ammonia, hydrochloric acid, and protoxide of nitrogen.—[S. S., chap. II.]

Give the preparation and properties of chlorine. Illustrate by symbols its action on a solution of protosulphate of iron.—[F. S., par. 528.]

Give the different modes of preparation, the composition by weight and by volume, the properties and uses of sulphurous acid.—[F. S., par. 545.]

How many grains of $Ba\,Cl, 2\,H\,O$ are required to precipitate all the sulphuric acid in 20 grains of $Na\,O\,S\,O_3$, $10\,H\,O$?

$$Ba = 68{\cdot}5 \qquad Na = 23{\cdot}0 \qquad Cl = 35{\cdot}5$$

—[F. S., chap. XIX.]

What is the principle on which is based Marsh's test for arsenic? Explain the modes of applying it, and the different precautions to be taken.—[Q. A., pars. 274 to 280.]

Give the preparation, properties, and decompositions of anhydrous hydrocyanic acid.—[F. S., par. 563.]

How are lactic and butyric acids prepared? Give the homologous series to which the latter belongs.—[F. S., par. 367, and S. S., par. 620.]

DIPLOMA OF C.E.

What are the laws which regulate chemical combination?—[F. S., pars. 127 to 150.]

How is chemical action characterised and distinguished from mechanical action? Give examples of each.—[F. S., pars. 24 to 28, and 125 to 127.]

What are the various sources from which sulphur is extracted? Mention the different processes for extracting and preparing it for use in the arts, as flower and roll sulphur. State its chief properties; its relations to heat;

and give the formulæ of the different acids it forms with oxygen.—[F. S., pars. 543 and 544.]

What are the formulæ of neutral sulphates of the protoxide and of the sesquioxide of iron? Why is the addition of sulphuric acid necessary in converting the former salt into the latter?—[F. S., pars. 445 and 446.]

Give in symbols the oxygen compounds of chlorine, and state shortly their properties.—[F. S., pars. 529 to 533.]

What are the characteristic reactions by which you would distinguish, by the blowpipe, ores of lead, bismuth, zinc, and antimony?—[Q. A., pars. 314, 325, 173, 174, and 262.]

How many cubic inches of oxygen can be obtained from 200 grains of chlorate of potash?

$$K = 39 \qquad Cl = 35{\cdot}5$$

100 grains of oxygen weigh 34·29 grains.

—[S. S., par. 4.]

Give the preparation and the properties of cyanogen.—[F. S., par. 562.]

Diploma of C.E., with Honours.

Explain shortly the atomic theory of Dalton.—[F. S., pars. 138 to 142.]

What is the law of combination among gases? How is the combining volume of a gas ascertained?—[S. S., chap. II.]

What is the supposed nature of ozone? How is it produced? Give its properties, and the means of detecting it in the atmosphere.—[F. S., page 266.]

By what means does the composition of the atmosphere remain uniform, notwithstanding the different densities of the gases composing it? What would be the relative rapidity with which oxygen and hydrogen mix with carbonic acid?—[F. S., pars. 174 to 182.]

DEPARTMENT OF SCIENCE AND ART.

EXAMINATION FOR SCIENCE CERTIFICATES.

Inorganic Chemistry.

1861.

I.*

Describe the usual processes for the preparation of chlorine.—[F. S., par. 528.]

How is nickel separated from cobalt?—[Q. A., par. 167.]

The formula usually adopted by chemists for felspar is $KO,\ SiO_3 + Al_2O_3,\ 3\,SiO_3$. In this formula $K = 39$, $Al = 13{\cdot}7$, $Si = 21$, $O = 8$. What is the formula of felspar if the following equivalents be taken?—

$K = 39$
$Al = 13{\cdot}7$
$Si = 28$
$O = 16$

—[F. S., chap. XX.]

II.

The specific gravity of nitrogen referred to that of hydrogen as unity is 14. What is the specific gravity of ammonia referred to that of hydrogen as unity? Give the method of calculation.—[S. S., pars. 119, 111, and 136.]

A salt has been found to contain, in 100 parts,—

Phosphorus	12·65
Magnesium	9·79
Nitrogen	5·71
Hydrogen	6·54
Oxygen	65·31
	100·00

What is the formula of the salt? The following equivalents to be used:—

Hydrogen	1	Phosphorus	31
Oxygen	8	Magnesium	12
Nitrogen	14		

Give details of calculation.—[F. S., chap. XX.]

III.

Give an outline of the manufacture of nitric acid, and state the quantities of sulphuric acid (HSO_4), nitrate of potassium (KNO_6), or nitrate of sodium ($NaNO_6$,) which are required to produce one pound of nitric acid (HNO_6).

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* Not more than one question in each section is permitted to be attempted.

$H = 1$
$O = 8$
$N = 14$
$S = 16$
$K = 39$
$Na = 23$

—[F. S., chap. XIX.]

How many volumes of oxygen gas are required to burn one volume of marsh gas and one volume of olefiant gas ; and how many volumes of carbonic acid gas are produced by their combustion?—[S. S., page 72, Exercise 86.]

1862.

I.

V volumes of sulphuretted hydrogen are decomposed by an excess of bromine; how many volumes of hydrobromic acid are generated by this reaction? State the mode of reasoning whereby the result has been arrived at.—[S. S., page 166, pars. 1 and 2.]

II.

The formula of alum is $KO, SO_3 + Al_2O_3, 3SO_3 + 24HO$, what is the composition of the salt in 100 parts? The following equivalents to be used:—

$H = 1$
$O = 8$
$S = 16$
$K = 39$
$Al = 13{\cdot}7$

Give such numerical details as will show the method of calculation.—[F. S., chap. XIX.]

Five volumes of a hydrocarbon ($Cn\,Hn$) are submitted to combustion. How many volumes of oxygen are required for its complete combustion, and how many volumes of carbonic acid gas are generated?—[S. S., page 73, Exercises 91 and 92, and Notes.]

III.

Give a definition of the terms acid, base, and salt.—[F. S., pars. 70 and 71.]

The formula of the mineral stilbite usually adopted by chemists is $CaO, SiO_3 + Al_2O_3, 3SiO_3 + 6HO$. In this formula the symbols have the following values:—

$H = 1$
$O = 8$
$Al = 13{\cdot}7$
$Si = 21$
$Ca = 20$

What is the formula of stilbite, if the following equivalents be used?—

H = 1
O = 16
Al = 27·4
Si = 28
Ca = 40

Give such numerical details as will show the mode of calculation.—[S. S., page 168, par. 4, and par. 884; and F. S., chap. XX.]

IV.

Describe one of the methods of estimating the amount of oxygen in atmospheric air.—[F. S., par. 520.]

The specific gravity of chlorine, referred to that of hydrogen as unity, is 35·5. What is the specific gravity of hydrochloric acid referred to that of hydrogen as unity?—[S. S., par. 136.]

Organic Chemistry.

1861.

I.

Describe the processes for transforming benzol into aniline.—[S. S., page 259, par. 3; page 407, par. 3; and Appendix I., page 414.]

An organic acid has been found to contain, in 100 parts,—

Carbon	60·87
Hydrogen	4·35
Oxygen	34·78
	100·00

The analysis of the silver salt of this acid has given the following result:—1·052 parts of the silver salt left, upon ignition, 0·4637 parts of metallic silver. What is the formula of the acid? Give details of calculation.—[F. S., chap. XX.]

III.

Express in formulæ the transformation of oxalic ether into oxamate of ethyl and oxamide.—[S. S., par. 827.]

Describe the method of preparing the chlorides of the acid radicals, and their deportment under the influence of water, alcohol, and ammonia.—[S. S., pars. 928, 929; page 422, par. 5.]

In determining the vapour density of an organic compound according to Dumas' process, the following observations were recorded:—

Temperature of air - - -	12° C.
Temperature of vapour - -	152° C.
Weight of glass globe filled with the vapour, *minus* weight of globe filled with air - -	0·386 grams.
Capacity of globe - - - -	292 c. c.
Barometer - - - - -	0·762 metres

100 cubic centimetres of air at 0° C., and bar. 0·760 metres, weigh 0·12932. What is the vapour density of the compound referred to hydrogen as unity? Give details of calculation.—[S. S., pars. 123, and 128 to 131.]

IV.

Give some examples of monatomic, diatomic, and triatomic alcohols. State their formulæ.—[S. S., pars. 553, 556 to 560, 734, 735, and 834.]

Describe a process by which alcohol may be converted into propionic acid, and acetic acid into glycolic acid.—[S. S., pars. 629, 631, and 805.]

Calculate the quantities of binoxide of manganese and hydrochloric acid which are necessary to convert, respectively, into chloroform ($C_2 H Cl_3$) and chloride of carbon ($C_2 Cl_4$) the quantity of marsh gas evolved by the distillation of 1 lb. of acetic acid ($C_4 H_4 O_4$) with an excess of lime. Give details of calculation.—[S. S., par. 637; and F. S., par. 528, and chap. XIX.

1862.

I.

What is soap?—[S. S., par. 836.]

How is acetic acid converted into acetic anhydride?—[S. S., par. 642.]

The analysis of a basic compound consisting of carbon hydrogen, and nitrogen, furnished the following results:—0·250 grams. of substance gave, on combustion, 0·632 grams. of carbonic acid ($C O_2$), and 0·337 grams. of water. The base forms, with hydrochloric acid and bichloride of platinum, a crystalline platinum salt. 0·500 grams. of double salt left, on ignition, 0·168 grams. of platinum. What is the per-centage composition of the base, and what is its formula? Give such numerical details as will show the method of calculation. Equivalents to be used :—

C = 12
H = 1
N = 14
O = 16
Pt = 98·7
Cl = 35·5

—[F. S., chaps. XIX. and XX.]

II.

How is benzoic ether prepared?—[S. S., par. 714.]

Describe the action of metallic zinc upon iodide of ethyl, and the products which are formed in the reaction. —[S. S., pars. 194 to 212.]

III.

Describe the composition and the preparation of acetone. —[S. S., pars. 507 and 508.]

IV.

What does the term substitution mean in chemistry? Give some examples of substitutions.—[F. S., par. 397; and S. S., par. 632.]

EXAMINATION OF SCIENCE SCHOOLS AND CLASSES.

Inorganic Chemistry.

1862.

Series I.[*]

What methods are generally employed for the preparation of hydrogen? Represent the reactions by diagrams or formulæ.—[F. S., par. 517.]

How is chlorine prepared?—[F. S., par. 528.]

What is the action of nitric acid upon copper?—[F. S., page 35, Exercise 73.]

What is the composition of water by weight and by volume?—[F. S., par. 518.]

How is bleaching powder prepared?—[F. S., par. 530.]

Express the preparation of nitric acid in formulæ.—[F. S., par. 522.]

What is the composition of the principal mineral from which lead is obtained?—[Q. A., par. 312.]

---

[*] Eight questions only are permitted to be attempted. They may be selected from Series I. or II., or from both; each question in Series I. is 8, and Series II. is 12·5.

The formula of oxide of silver is $Ag\,O$, the equivalent of silver is 108, the equivalent of oxygen is 8. How many pounds of oxide of silver are necessary to make 100 lbs. of oxygen?—[F. S., chap. XIX.]

What is the source of hydrochloric acid, and how is it prepared?—[F. S., par. 533.]

1863.

What is the composition of hydrochloric acid by weight and by volume?—[S. S., par. 104.]

How is nitrogen prepared?—[F. S., par. 519.]

How is ammonia prepared?—[F. S., par. 527.]

What is meant by the term *aqua regia?*—[F. S., par. 534.]

How is manganese detected in a mineral?—[Q. A., par. 171.]

In what state is sodium found in nature?—[Q. A., par. 113.]

Describe the preparation, composition, and properties of carbonic acid.—[F. S., par. 555.]

Describe the different modifications of carbon.—[S. S., par. 192.]

In what state does tin occur in nature?—[Q. A., par. 248.]

Series II.

1862.

How are barium, strontium, and calcium detected when mixed?—[Q. A., par. 133.]

What is the composition of gunpowder, and what reaction takes place during its explosion?—[S. S., page 2, Exercise 9.]

How many compounds of phosphorus and hydrogen are there, and how are they obtained?—[F. S., par. 553.]

How are the oxides of nitrogen prepared?—[F. S., pars. 521 to 526.]

A substance has been found to contain,—

Arsenic . - - - - - -	65·22
Oxygen - - - - - - -	34·78
	100·00

The combining number of Arsenic is 75.
„ „ Oxygen is 8.

What is its formula? Give details of calculation.—[F. S., chap. XX.]

The formula of sulphate of copper is $Cu\,S\,O_4 + 5\,H\,O$. What is its per-centage composition?

Combining number of		Copper	31·5
„	„	Sulphur	16
„	„	Oxygen	8
„	„	Hydrogen	1

Give details of calculation.—[F. S., chap. XIX.]

1863.

State the composition and the preparation of the most important compounds of sulphur with oxygen.—[F. S., pars. 544 to 547.]

Give an outline of the method of preparing phosphorus. Represent in formulæ the reactions involved in this preparation.—[F. S., par. 549.]

How are calcium, magnesium, and iron detected when occurring together in solution?—[Q. A., page 134, table VII., pars. 3, 5, and 6.]

The formula of crystallized carbonate of sodium is $Na\,C\,O_3 + 10\,H\,O$. What is its per-centage composition? Give such numerical details as will show the mode of calculation.

$H = 1$ | $C = 6$
$O = 8$ | $Na = 23$

—[F. S., chap. XIX.]

How many pounds of copper are necessary to prepare 100 pounds of crystallized sulphate of copper ($Cu\,S\,O_4 + 5\,H\,O$)?

$H = 1$ | $S = 16$
$O = 8$ | $Cu = 31{\cdot}7$.

—[F. S., chap. XIX.]

A substance has been found to contain,—

Tin - 78·67
Oxygen 21·33
100·00

$Sn = 59$
$O = 8$

What is its formula? Give such numerical details as will show the mode of calculation.—[F. S., chap. XX.]

Organic Chemistry.

Series I.

1862.

What is the action of chlorine upon olefiant gas?—[S. S., par. 525.]

In what relation does aldehyde stand to alcohol and acetic acid?—[S. S., pars. 478 and 479.]

Give examples of monobasic, bibasic, and tribasic organic acids.—[S. S., pars. 600 to 603, 620, 812, and 881.]

What is the action of nitric acid upon benzol?—[S. S., page 259, par. 3.]

What is meant by the term "series of fatty acids"?—[S. S., par. 619.]

What is the action of excess of baryta on benzoic acid at a high temperature?—[S. S. 693, Exercise 2.]

What are homologous bodies? Give some examples.—[S. S., page 278, Appendix A.]

1863.

What is the formula of acetic acid?—[S. S., par. 620.]

Describe a method of preparing olefiant gas.—[S. S., par. 522.]

How is iodide of ethyl prepared?—[S.S., par. 910.]

State the composition of urea.—[S. S., pars. 1057 to 1063.]

What is soap?—[S. S., par. 836.]

What is the action of chlorine on acetic acid?—[S. S., par. 632.]

How is sugar converted into alcohol? Represent the reaction in an equation.—[F. S., pars. 364 and 365.]

Give some examples of organic bodies which may be referred to the type water.—[S. S., page 248.]

Series II.

1862.

What is the action of heat and dehydrating agents on formiate of ammonium and acetate of ammonium.—[S. S., par. 1013.]

What is the action of solution of ammonia upon oxalic ether? What is the constitution of the principal product?—[S. S., par. 827.]

Give an example of a diatomic alcohol, and what are the acids that may be derived from it?—[S. S., par. 756.]

How is benzoic alcohol prepared?—[S. S., par. 595.]

What is the action of chloride of benzoyl on dry carbonate of ammonium, and what is the constitution of the product?—[S. S., page 422, 5th Example.]

A compound has been found to contain,—

Carbon	40·00
Hydrogen	6·67
Oxygen	53·33
	100·00

What is its formula? Combining number of carbon, 6; hydrogen, 1; oxygen, 8. Give details of calculation.—[F. S., chap. XX.]

What are simple, mixed, and compound ethers, and in what relation do they stand to water?—[S. S., pars. 384 and 710.]

1863.

Describe the method of transforming benzol into aniline.—[S. S., page 259, 3rd example; and page 407, 3rd example.]

What are the products of the action of sulphuric acid upon alcohol?—[S. S., par. 571.]

Give examples of primary, secondary, and tertiary monamines.—[S. S., par. 972.]

A compound has been found to contain,—

C	58·53
H	7·32
N	34·15
	100·00

H = 1
C = 6
N = 14

What is its formula? Give such numerical details as will show the mode of calculation.—[F. S., chap. XX.]

Give examples of monatomic, diatomic, and triatomic alcohols.—[S. S., pars. 553, 559, 735, and 834.]

Calculate the per-centage of carbon, hydrogen, and oxygen contained in benzoic acid ($C_{14}H_6O_4$).

H = 1 C = 6 O = 8

Give such numerical details as will show the method of calculation.—[F. S., chap. XIX.]

Describe the several methods of ascertaining the presence of hydrocyanic acid.—[Q. A., pars. 452 to 455.]

State the preparation and composition of mercaptan.—[S. S., par. 366.]

THE END.

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